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The use of polymers from furfural in the fabrication of molded products

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NOTE TO USERS

THE USE OF POLYMERS FROM FURFURAL IN THE FABRICATION OF MOLDED PRODUCTS

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INTRODUCTION

An outstanding event of the year 1933 was the celebration of the World's Fair in Chicago, marking one hundred years since the founding of the city, and one hundred years of scientific achievement. One of the many products displayed at the "Century of Progress" celebrated its centenary as well. This product is furfural, which was discovered one hundred years ago by Dobereiner.

In the one hundred years that have past furfural has come from a laboratory curiosity to an industrial commodity. It was first thought to be an interesting but useless oil, but at present finds uses ranging from a purifying and preserving agent to the basis for a series of interesting plastic materials. In 1929, 1,500,000 pounds of furfural were produced. Since furfural is manufactured from waste oat hulls, the production is limited only by the demand for the compound, and as research reveals new uses, the production of furfural will increase. The production of furfural is one of the many examples of the manner in which the problem of the utilization of agricultural wastes is being solved by chemical means.

Furfural is a water white oily liquid, having a burnt sugar odor. Impurities and polymers usually present produce a straw-yellow color. It boils at 161 ^{o}C., and has a specific gravity of 1.159 at 20 ^{o}C. Its many peculiar properties result from the fact that it contains two char-

acteristic groups, the furane group, and the aldehyde group. Although furfural possesses the properties of each of these groups, the fact that both groups are present has its effect in producing properties found only in this material. Research is being carried out, both in finding new uses for furfural, and in the determination of its properties. It has been predicted that in the near future a system of furane chemistry comparable to the system of benzene chemistry will be known.

The purpose of this thesis is to add to the uses of furfural, and in particular to utilize it to greater advantage in the manufacture of plastics.

HISTORICAL

As has already been noted, furfural was discovered by Dobereiner about a century ago (13). To Stenhouse, however, goes the credit for first obtaining any quantity of the compound (48). In 1840 he produced a yellowish oil, which he named "oil of ants," by treating oatmeal and sawdust with sulphuric acid. He determined the physical constants of the compound, but later work by other investigators showed that his results were somewhat inaccurate. Correct values of the various constants are given below.

Density (20 C.)	1.159	(53a)
Melting point	-38.7	(53b)
Dielectric constant (20 C.)	41.9	(53c)
Boiling point	161.7	(53d)
Refractive index (D line sodium)	1.52608	(17)

Furfural remained a laboratory curiosity until a process for producing it on a commercial scale was perfected in 1922. Since that time, it has found a steadily increasing application in industry, and as a result its price has decreased until furfural is the cheapest aldehyde to be had.

Furfural is used in a wide variety of processes. In some degree it has been substituted for formaldehyde in the preparation of embalming fluids, and finds special use in the preservation of anatomical specimens for use in the study of veterinary medicine (5). Furfural finds extensive use as a selective solvent for the purification of anthracene and wood rosin. A good method for the purification of anthracene

has been in demand for some time, due to the fact that anthracene is the raw material for the production of anthraquinone, which in turn is the basic substance from which the dye alizarine is prepared. The crude anthracene contains large amounts of phenanthrene and carbazole. Formerly the phenanthrene was taken out by solvents and most of the carbazole was removed by catalytic oxidation; however, by the use of furfural, it is possible to remove both of these impurities without destroying them. The process consists of dissolving the crude anthracene in hot furfural, which readily dissolves all three of the main constituents of the crude anthracene. On cooling, the carazole and phenanthrene remain in solution, while a considerable portion of the anthracene crystallizes out. One such crystallization yields a product containing 92-95% anthracene, together with only 2% of carbazole. The recovery of anthracene is about 96%. The use of furfural as a selective solvent in the purification of anthracene is covered by several patents (23, 39).

Wood rosin is also purified by utilizing the selective solvent action of furfural. The object of the purification is to remove color, which is objectionable when the rosin is to be used in the preparation of varnishes, or as a sizing agent in the paper pulp industries. The color is produced by color bodies of two types; (1) those producing the characteristic ruby red color and (2) those reacting with alkali to form red products. Two solvents are used together--furfural

and gasoline. It has been found that the impurities producing color in the resin are soluble in furfural, whereas the rosin itself is more soluble in gasoline. Since at low temperatures (25 °F.) gasoline and furfural are practically immiscible, by cooling a solution it is possible to draw off the gasoline layer, distill it, and recover a light colored rosin. The furfural is also recovered from the color bodies by distillation. This process is being used on a commercial scale, one plant circulating 80,000 gallons of furfural. Furfural losses are less than 1%. Patents have been issued (24, 25) covering the use of furfural in the purification of wood rosin.

A process has been suggested (14) to utilize the solvent action of furfural in the purification of hydrocarbon oils.

In addition to its uses as a preservative and selective solvent, furfural finds application in the manufacture of plastics.

The possibilities of using furfural in preparing synthetic resins and plastics have long been appreciated. When one is working with furfural, extreme care is necessary if the desired reaction is to take place, and the worker is not to be rewarded with a sticky tar or black solid at the close of his efforts to produce his compound. This property might in some degree be expected, since furfural is an aldehyde, and this class of compounds is known to possess the property

of readily polymerizing. The property of furfural of forming gums and resins when boiled with caustic and acids was noted by Stenhouse as early as 1840 (48). Although several experimenters found gums similar to those found by Stenhouse later in the nineteenth century, not much progress was made in the use of furfural until 1914. Meunier (36) was one of the first to work on the problem of making resins. He obtained a plastic by treating furfural with aniline or acetone in the presence of caustic soda or ammonia. His main object was the production of resins to be used in the varnish industry. A very large number of compounds were investigated by Beckman and Dehn (4) in order to find their value in the production of furfural plastics. Among the reagents they tried are ortho, meta and para cresol, crude cresols, hyroquinone, pyrogallol, picric acid, menthol, and alpha and beta naphthol. The mentioned compounds are but a few of those tried. Beckman and Dehn reported that best results are attained when using phenol, crude cresol, and beta naphthol. In some of their resins they used hydrochloric acid as a catalyst, and in others a basic catalyst was used.

The fact that furfural is an aldehyde makes it susceptible to reaction with several classes of compounds. The most important is the phenol class, which includes such compounds as phenol itself and cresol. Furfural also reacts with ketones, particularly acetone, to form resins. Urea and its derivatives react with furfural, forming resins similar

to "Beetle" resin. Furfural possesses the property of reacting with itself, or polymerizing, and can also react with other aldehydes.

The commercial success of Bakelite and other similar resins has been the stimulus resulting in a large amount of work on resins produced by a condensation of furfural and a phenol type compound. The Bakelite Corporation holds a patent on a process by which furfural is condensed with cresol or phenol to yield a reactive resin, to which is added an alkaline earth oxide such as lime, and a hardening agent, such as hexamethylene tetramine (3). A coating compound is produced (34) by condensing furfural with a phenolic compound in the presence of tung oil. The resultant solution is used as an impregnating agent for fibrous materials. Sheets of cloth or paper so impregnated may be molded under heat and pressure to form durable laminated products.

A resin produced utilizing the furfural derivative furfuramide is described (11). Furfural is heated with a phenolic body such as cresylic acid, and is heated further with a methylene containing body, such as formaldehyde. The excess methylene groups are then utilized by adding furfuramide, and a resin results. The reaction between cresols and furfural may be carried out in several steps, as suggested in a patent held by the Bakelite Corporation (2). The reaction first takes place in the presence of a limited amount of a basic condensing agent, such as lime. At the

close of this procedure the resin formed is plastic, and other materials may be added, after which the reaction is completed by adding more lime and heating. Another patent (18) suggests the arresting of the reaction at some intermediate stage in order to dehydrate the resin, and add hardening materials. Emil Novotny (41) carries out a similar reaction in steps, by holding the first reaction temperature below 350 °F. The result of this low temperature heating is a fusible resin, which by further heating is converted into an infusible form. Furfuramide is specified as a hardening agent in a patent by Novotny (42), and he utilizes a furfural resin as a material for making phonograph records and laminated materials in another patent (40). A Bakelite type furfural resin is produced by Carleton Ellis (16) by a reaction between phenol and furfural in the presence of sodium carbonate. The resin produced is hardened by means of hexamethylene tetramine and some fixed alkali.

A furfural-cresol resin is produced by a novel method proposed by O. R. Sweeney (49). Ground corn cobs are digested with cresol in the presence of a mineral acid. Furfural, resulting from the action of the acid on the corncobs, unites with the cresol to form a resin, while the cellulosic pulp remaining from the corncobs acts as a filler for the resin. W. D. Harris found on further investigation of this resin, that alkaline catalysts could also be used, but that the resin produced was always fusible, and did not become converted to

an infusible form by the application of heat (20). All the resins of the corncob-cresol type were found to be somewhat attacked by water, a drawback attributed by Harris to the presence of soluble sugars and their derivatives in the resin.

A reaction producing resins is that between aldehydes and urea. Commercial application of this reaction may be seen in the production of "beetle" or pollapas resin from urea or its derivatives and formaldehyde. If the reaction is carried out using furfural in place of formaldehyde, resins are also produced. Several methods of producing the resin are employed. A black compound resembling ebonite is produced by refluxing furfural with urea, with or without the use of a catalyst or solvent (26). In some cases other aldehydes or amino compounds are added, or the reaction may be carried out in stages, to permit ready addition of fillers or to accomplish dehydration. A Swiss patent covers the use of thio-urea, aniline, alpha or beta naphthylamine and meta or para phenylenediamine in the production of urea-furfural resins (27). Thio-urea and furfural react to produce an infusible and insoluble resin (28). The reaction may be modified by the use of a contact agent, a diluent or solvent. The use of acidic or basic catalysts in the furfural-urea reaction is mentioned in a recent patent (43). This reaction may also be carried out in steps.

Reactions between ketones and furfural produce resins.

Of particular interest in connection with this thesis is the formation of a resinous mass in the reaction between acetone and furfural. The first observations on this reaction were made by Claison and Ponder (12), who produced a light yellow oil which they named "furfural acetone." This oil upon standing became a resinous mass. Meunier allowed furfural and acetone to react in the presence of strong alkaline catalysts by which method he produced a light yellow resin (37). Mains and Phillips, duplicating the work of Meunier, found that by carrying out the reaction at higher temperatures, the resin that was produced would have a higher melting point (33). Resins were produced having a melting point of 100 °C. and were recommended for use as varnish resins. L. T. Richardson (45) in his process for producing the resin, follows much the same procedure as Meunier, except that the dry resin is mixed with acid condensing agents and fillers, and is then hot molded under pressure to produce a plastic. Furfural-acetone resins were tested by Matlack (35) for use as an impregnating agent for synthetic lumber.

The ease with which furfural polymerizes may be utilized in the production of resins. Various aldehydes may be used with furfural in these reactions (31). Infusible black reaction products result from the reaction of furfural with other aldehydes such as acetaldehyde, para aldehyde, formaldehyde, benzaldehyde and crotonaldehyde. Inorganic acids such as hydrochloric acid are used to aid the reaction. These

polymers with other aldehydes may also be produced in the presence of diluents or solvents (30). Furfural derivatives such as furfuryl alcohol may be used (52). Various metals and their salts are claimed to have a polymerizing action on furfural (51). Salts such as ferric chloride, aluminum chloride, lead acetate and iron pyromucate are mentioned, as are metals such as iron, nickel, lead, magnesium, zinc and tin. A similar patent (46) mentions the use of phosphoric acid, hydrochloric acid, bromine, sulphur dichloride and sulphuric acid in the preparation of resins by the polymerization of furfural.

It has been suggested that furfural be substituted for formaldehyde in the curing of casein plastics such as galalith. This use of furfural was first studied by Campbell (9), who produced a satisfactory molding compound by mixing casein and furfural, which on the application of heat and pressure resulted in a brown resin. The work with various modifications is the subject of several patents (22, 47). The process has its disadvantages in that the resins produced always have a dark brown or black color; also the use of formaldehyde instead of furfural permits the article to be hardened by immersion in a solution of formaldehyde. Articles could not be successfully cured by similar treatment with furfural.

Resinous derivatives of furfural are formed by a variety of reactions which do not belong to any group or type reaction. A resin of particular interest in connection with this thesis

is one produced by passing ammonia into an aqueous solution of furfural (33). The hydrofuramide formed was removed by filtering and was then heated for one hour. Subsequent investigation (50) found the resin to be impure furfurin.

A resin is produced by the reaction between furfural and acetic acid, in the presence of acidic condensing agents (29). The product is a hard, gumlike mass, which is resistant to acids and alkalies. A suggested use is the impregnation of wood, paper, or other cellulosic products before the final hardening of the material occurs. A Canadian patent (38) has as its subject a resin formed by the reaction of equimolecular parts of furfural and para toluene sulfonamide. The reaction takes place in the presence of three percent of a catalyst such as soda ash, at a temperature of 150 °C. maintained for eight hours.

In the presence of hydrochloric acid, lignin and furfural react to form a black resinous body (44). Ellis (15) produces a resin by dissolving nitrocellulose in furfural, and resinifying the solution by means of acids. The resultant material may be poured into molds or formed into thin films.

A new type of resin produced from furfural has been developed at Iowa State College. All the data concerning this particular resin are found in theses which are as yet unpublished (1, 6, 7, 19). The early work on the resin was done by P. F. Bruins (6). While attempting to prepare a furfural derivative for use as a rubber accelerator, it was

found that the addition of hydrochloric acid to a solution of furfurin in furfural caused the solidification of the liquid into a hard, black, shiny mass. Further work was done to improve the material, with the following results:

(1) The effect of varying the hydrochloric acid percentage. It was found that the correct ratio was about one third acid to two thirds furfural solution by volume. More recent work has shown that satisfactory materials may be obtained by using twenty to twenty five percent of concentrated hydrochloric acid by volume. A less acidic product is obtained with no decrease in strength.

(2) The effect of using technical or redistilled furfural. It was found that the use of redistilled furfural did not yield a better product.

(3) The effect of varying the furfurin content. This was controlled by varying the time of treatment with ammonia. It was found that a treatment of about 90 minutes was optimum. This length of time corresponds to a furfurin content of 19.3%.

(4) The effect of polymerizing agents other than hydrochloric acid. The use of hydrochloric acid gas was attempted, but did not result in a desirable product. Small amounts of various salts were added to the furfurin solution, without obtaining good results. Various organic acids were used without success. Sulphur dichloride failed to give good results. Sulphuric acid gave good results, but could not be

used in the concentrated form, due to localized setting. Sodium and potassium hydroxide were found to have no value as polymerizing agents. Experiments suggested by the work of Losanitsch (32), using the silent electric discharge, were carried out, but the results obtained were not conclusive.

(5) The use of fillers was studied. Mixtures were made up containing such fillers as corncob flour, cornstalk flour, wood flour, asbestos fiber, oathull residue, sawdust, plaster of paris and gypsum, and a filler produced by grinding pieces of hardened plastic.

(6) Various methods of reducing acidity and preventing checking were tried out. These included storing in contact with flake caustic, treatment under vacuum with ammonia, extracting with solvents, and baking the finished product. The baking process was the most promising, the time and temperature of baking varying with the size of the article in question.

(7) The physical properties of the plastic are presented.

(8) Commercial applications for the plastic are suggested, and a plan for the production of golf tees is given in some detail.

The plastic at the end of the series of experiments performed by P. F. Bruins still had several serious defects. Chief of these was the high acidity exhibited by the material, and the fact that the plastic cracked when formed into anything other than very small pieces. R. W. Bruins (8) attempted

to solve the cracking problem by incorporating calcium chloride into the plastic, as water was suspected of being the cause of the cracking. No beneficial results were obtained, other than a slight increase in tensile strength. Experiments were then carried out to determine if cracking might be eliminated by keeping the article out of contact with air. A coating of a drying oil, such as tung or linseed, was found to eliminate cracking to some degree. Excellent results were obtained, however, by coating the article with paraffin, and specimens have been kept without checking for almost four years by this method.

Up to this time the only gas with which furfural had been treated was ammonia. Experiments were conducted to determine the effect of other gases. The first gas selected was oxygen, and a beneficial effect was noted on the properties of the plastic by the addition of furfural treated with oxygen. A series of tests were made, varying the time and method of treatment with oxygen, the amount of furfural treated with oxygen added, and the age of the samples, which were kept from cracking by the paraffin method. The data resulting from the series of tests showed that the addition of 20% by volume of furfural treated with oxygen for two hours at 110 ^{o}C. and under atmospheric pressure, increased the tensile strength to over 1000 pounds per square inch. Maximum strength was attained in about one week. This time could be diminished by

treating the furfural with oxygen for longer periods. Furfural was treated with oxygen under pressure, but the resultant solution was not more effective than the solution produced under atmospheric pressure.

Since the production of golf tees from the plastic was an interesting commercial possibility, a machine for the production of golf tees was designed and constructed. This machine is a device for automatically filling suitable molds with the liquid mixture at a rate of about seventy five per minute.

EXPERIMENTAL WORK

1. STUDIES ON THE FURFURAL-FURFURIN PLASTIC

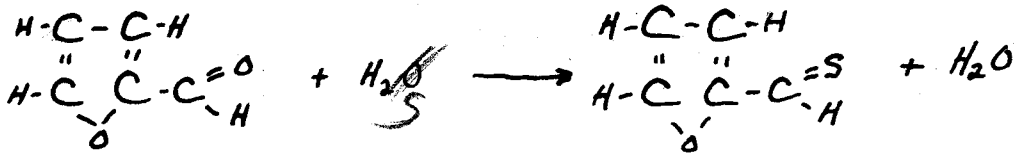
A. The treatment of furfural with hydrogen sulphide.

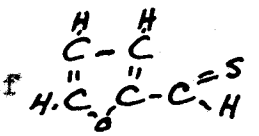
1. Reason for testing H_2S-furfural solutions.

The investigation of the effect of hydrogen sulphide on furfural was the result of studies on the effects of ammonia and oxygen on furfural. Use of ammonia in the furfural plastic resulted in the formation of a hard material, which solidified rather rapidly in comparison with furfural-acid mixtures containing no ammonia; furfural treated with oxygen and acid resulted in a soft carbon-like material of no great value in itself, but the addition of furfural treated with oxygen to the furfural-furfurin plastic resulted in a material having superior tensile strength and less tendency toward shrinking and cracking. The treatment of furfural with hydrogen sulphide presented the possibility that other beneficial effects might be obtained.

2. Reactions.

The idea of treating furfural with hydrogen sulphide is not a new one. Work in this laboratory revealed the fact that sulphur derivatives of furfural may be obtained by the treatment of aqueous solutions of furfural with hydrogen sulphide (6). The reaction proceeds according to the following plan:



Furfural polysulphide is probably a polymer of  . It is a gummy material, yellow when fresh, but turning dark on standing in the air, and having an unpleasant characteristic odor. It was found to be an efficient accelerator for the vulcanization of rubber. (6)

All this previous work differed, however, from the treatment of furfural with hydrogen sulphide under discussion, in that water solutions of furfural were used, while in the work being presented the technical (almost anhydrous) grade of furfural was heated and dry hydrogen sulphide was bubbled through the liquid. After treatment the liquid was probably a solution of furfural polysulphide in furfural.

3. Method of procedure.

a. Tensile tests. The determination of the tensile strength of test briquets afforded a means of comparing the various mixtures used. The samples were molded in the form of tension briquets, having a minimum cross section of one square inch, so that the strength in pounds per square inch could be obtained directly. The molds used were two-piece brass molds, such as are commonly used in making tension test briquets of concrete mixtures. Due to the corrosive action of the materials used in these experiments, it was found necessary to coat the molds with paraffin, to prevent both corrosion and adherence of the sample to the mold. The testing machine used was an Olsen cement testing machine,

such as is used for testing concrete mixtures. The procedure followed was similar to the one used in the determination of the effect of oxygen on furfural (8).

b. Materials used. The furfural used in these studies was supplied gratis through the courtesy of the Quaker Oats Company. It was of the technical grade, and was withdrawn as needed from a fifty five gallon steel drum. If treated with ammonia, the furfural was heated to 110 °C. and anhydrous ammonia from a cylinder of the liquified gas bubbled into the furfural until a 20% solution of furfurin in furfural was obtained. Hydrogen sulphide was obtained by the treatment of ferrous sulphide with dilute hydrochloric acid in a Kipp generator. The gas was bubbled through the furfural heated to 110 °C. for the desired time. The hydrochloric acid used in making up the samples was concentrated C. P. acid, sp. g. 1.195, 39% HCl, unless otherwise stated.

c. Plan of testing. In the determination of the effect of hydrogen sulphide on furfural, two groups of tests were made. The first group contained furfural treated with hydrogen sulphide, and hydrochloric acid. Four series of tests were made in this group, varying the time of treatment with hydrogen sulphide from one half to three hours, and varying the hydrochloric acid content from five to thirty percent of the total volume of the mixture. In the second group of tests, furfural treated with ammonia was added to

the two previously mentioned constituents. In this group, the time of treatment with hydrogen sulphide was varied from one to three hours, and the amount used from 70 to 10% of the total volume of the mixture. The furfural treated with ammonia had a furfurin content of 20%, and was added in amounts varying from 10 to 70%. A constant percentage of 20% of concentrated hydrochloric acid was used throughout this group of tests.

d. Data. The data obtained in these tests are tabulated in Table 1. Under the heading "Type of Break" will be found four different terms descriptive of the manner in which the specimen failed. The term "Square" indicates that the specimen broke squarely across at the point of minimum cross section. "Rough" indicates that the sample broke at about the middle section, but that the break was uneven. The term "Jaw" implies that the specimen failed at the points where the jaws of the testing machine gripped it. "Defect." is the term applied if the test piece breaks along a crack or other defect in the sample.

TABLE NO. I

TENSION TESTS OF BRIQUETS

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S treated	Furf. NH_3 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
1 a	1	90	0	10	7	150	Jaw	
b					10	225	Jaw	
c					13	250	Jaw	
d					17	200	Jaw	
e					20	200	Square	
2 a	1	80	0	20	7	300	Square	
b					10	270	Rough	
c					13	300	Rough	
d					17	450	Square	
3 a	1	75	0	25	7	225	Rough	
b					10	225	Jaw	
c					13	240	Jaw	
d					17	300	Jaw	
e					20	250	Square	
4 a	1	95	0	5	7	100	Jaw	
b					10	100	Jaw	
c					13	100	Jaw	
d					17	100	Jaw	
55 a	1	85	0	15	7	400	Jaw	
b					10	850	Jaw	
c					13	800	Jaw	
d					17	750	Jaw	
e					20	450	Square	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S treated	Furf. NH_3 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
6 a	1	70	0	30	7	200	Square	
b					10	300	Square	
c					13	200	Jaw	
d					17	250	Rough	
7 a	.5	95	0	5	6	0	Square	
b					9	0	Square	
c					12	0	Square	
d					16	0	Square	
8 a	.5	90	0	10	6	0	Jaw	
b					9	0	Jaw	
c					12	50	Square	
9 a	.5	85	0	15	6	50	Square	
b					9	100	Jaw	
c					13	175	Rough	
d					16	400	Square	
10 a	.5	80	0	20	6	100	Square	
b					9	300	Jaw	
c					13	225	Jaw	
d					16	125	Defect.	
11 a	.5	75	0	25	6	270	Jaw	
b					9	270	Jaw	
c					13	300	Jaw	
d					16	300	Jaw	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S treated	Furf. NH_3 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
12 a	.5	70	0	30	6	200	Square	
b					9	200	Jaw	
c					13	175	Jaw	
d					16	175	Square	
e					19	200	Square	
13 a	2	95	0	5	6	100	Square	
b					9	175	Jaw	
c					13	75	Defect.	
d					16	0	Defect.	
14 a	2	90	0	10	6	340	Jaw	
b					9	400	Jaw	
c					13	200	Jaw	
d					16	950	Jaw	
e					19	350	Jaw	
15 a	2	85	0	15	5	360	Square	
b					8	200	Square	
c					12	575	Jaw	
d					15	600	Jaw	
e					18	450	Square	
16 a	2	95	0	5	2	0	Material still soft.	
b					5	0	Still soft. Tech.	
c					9	50	Square	HCl used.
d					12	50	Square	
e					15	0	Defect.	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S	Furf. NH_3	NCl				
	hrs.	%	%	%	days	lbs/sqin		
17 a	2	90	0	10	2	0	Material	still soft.
b					5	20	Jaw	Tech. HCl
c					9	50	Jaw	used.
d					12	60	Jaw	
18 a	2	85	0	15	2	0	Material	still soft.
b					5	100	Jaw	Tech. HCl
c					9	110	Square	used.
d					12	130	Jaw	
e					15	200	Jaw	
f					21	300	Jaw	
19 a	2	80	0	20	Inferior material. Not tested. Tech. HCl used in Nos. 19,20,21			
20 a	2	75	0	25	Inferior material. Not tested.			
21 a	2	70	0	30	Inferior material. Not tested.			
22 a	3	95	0	5	1	75	Square	
b					4	50	Jaw	
c					7	75	Jaw	
d					13	125	Jaw	
e					17	100	Square	
23 a	3	90	0	10	4	110	Jaw	
b					7	100	Jaw	
c					13	500	Jaw	
d					17	275	Defect.	
e					20	700	Jaw	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S	Furf. NH_3	HCl				
	hrs	%	%	%	days	lbs/sqin		
24 a	1	70	10	20	5	250	Rough	
b					9	350	Jaw	
c					12	350	Jaw	
d					15	850	Square	
25 a	1	60	20	20	5	375	Jaw	
b					9	450	Jaw	
26 a	1	50	30	20	4	450	Jaw	
b					8	930	Jaw	
c					11	+1000	Failed to break.	
d					14	850	Jaw	
e					25	800	Jaw	
27 a	1	40	40	20	4	700	JJaw	
b					8	630	Jaw	
c					11	750	Jaw	
d					14	+1000	Failed to break.	
e					25	850	Jaw	
28 a	1	30	50	20	4	650	Jaw	
b					8	850	Jaw	
c					11	850	Jaw	
d					14	900	Jaw	
e					25	950	Jaw	
29 a	1	20	60	20	4	500	Jaw	
b					8	400	Jaw	
c					11	550	Rough	
d					14	900	Square	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S	Furf. NH_3	HCl				
	hrs.	%	%	%	days	lbs/sqin		
30 a	1	10	70	20	4	350	Square	
b					8	450	Square	
c					11	625	Rough	
31 a	1	20	60	20	4	550	Jaw	
b					8	300	Jaw	
c					11	350	Square	
d					14	900	Square	
e					25	+1000	Failed to break.	
32 a	2	10	70	20	4	300	Jaw	
b					7	500	Jaw	
c					10	550	Jaw	
d					21	700	Jaw	
33 a	2	20	60	20	4	350	Jaw	
b					7	500	Jaw	
c					10	550	Jaw	
d					21	650	Jaw	
e					23	700	Jaw	
34 a	2	30	50	20	4	350	Jaw	
b					7	500	Jaw	
c					10	625	Jaw	
d					21	750	Jaw	
e					23	750	Jaw	

Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S treated	Furf. NH_3 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
35 a	2	40	40	20	4	400	Jaw	
b					7	500	Jaw	
c					10	600	Jaw	
d					21	800	Jaw	
36 a	2	50	30	20	4	500	Square	
b					7	500	Jaw	
c					10	775	Jaw	
d					21	800	Jaw	
37 a	2	60	20	20	4	500	Jaw	
b					7	800	Jaw	
38 a	2	70	10	20	4	600	Square	
b					21	800	Square	
39 a	3	10	70	20	4	300	Jaw	
b					9	500	Jaw	
c					20	500	Jaw	
d					22	550	Square	
e					24	450	Square	
40 a	3	20	60	20	4	400	Jaw	
b					9	450	Jaw	
c					20	650	Jaw	
d					22	600	Jaw	
e					24	600	Jaw	

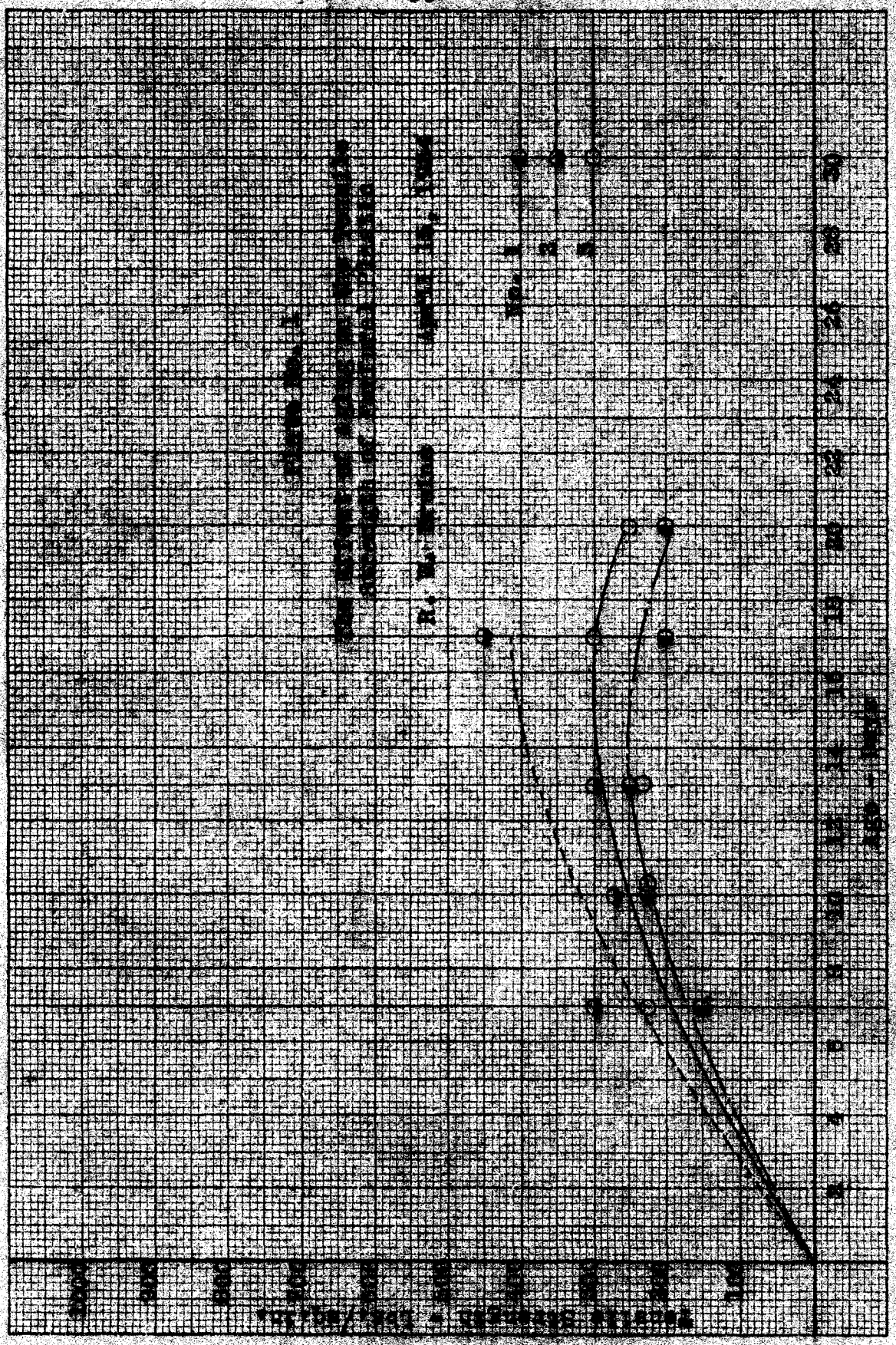
Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of Break	Remarks
		Furf. H_2S treated	Furf. NH_4 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
41 a	3	30	50	20	4	350	Jaw	
b					20	700	Jaw	
c					22	600	Jaw	
d					24	600	Jaw	
e					29	650	Jaw	
42 a	3	40	40	20	4	400	Jaw	
b					20	600	Jaw	
c					22	600	Jaw	
d					24	600	Jaw	
43 a	3	50	30	20	4	400	Square	
b					20	600	Jaw	
c					22	650	Square	
d					24	600	Jaw	
e					29	500	Jaw	
44 a	3	60	20	20	4	450	Jaw	
b					20	400	Square	
c					22	450	Jaw	
d					24	550	Square	
e					29	600	Square	
45 a	3	70	10	20	Overheated when made. No tests made.			
46 a	2	60	20	20	3	150	Square	
b					19	800	Jaw	
c					21	650	Jaw	
d					23	300	Defect.	

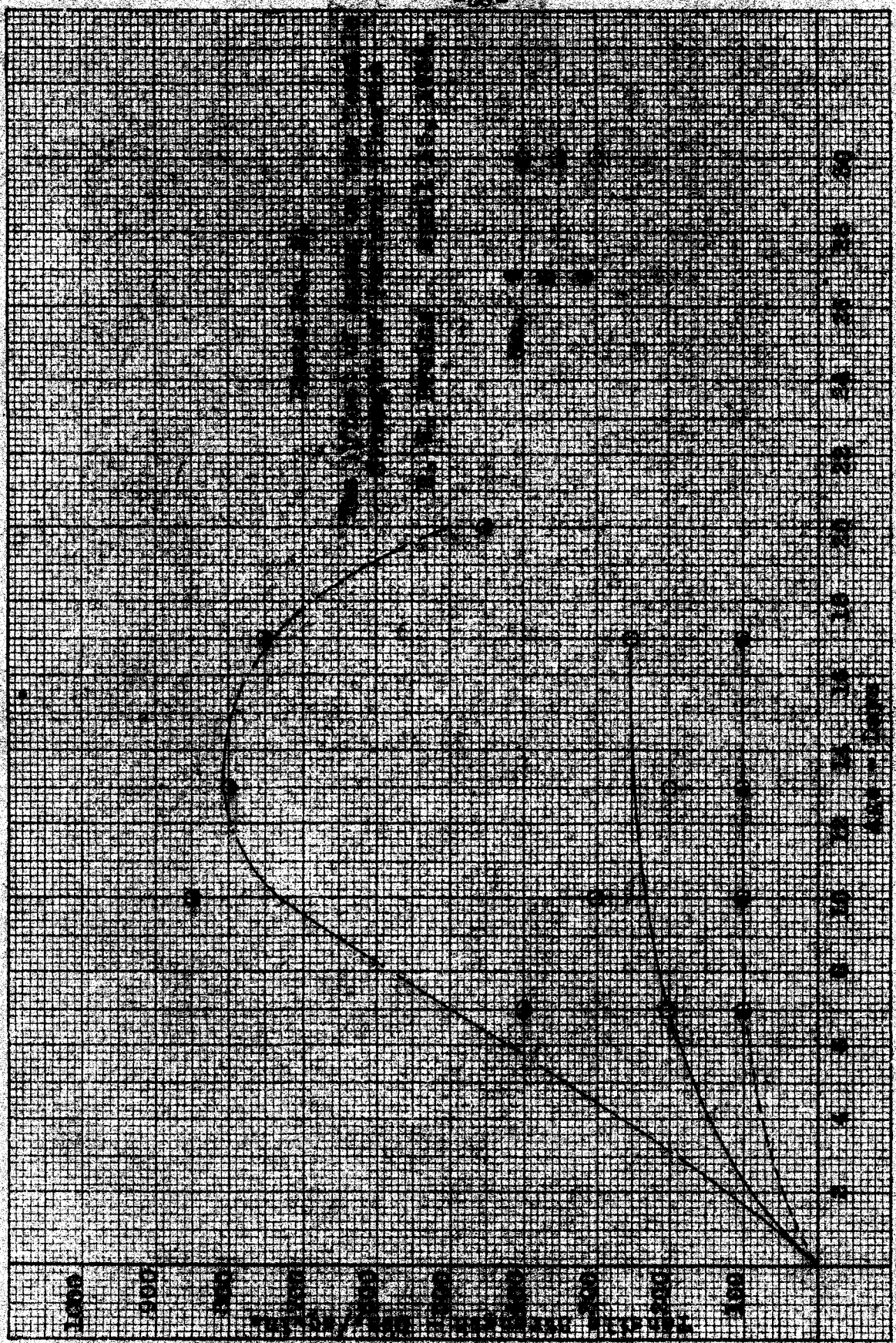
Table No. 1; continued.

No.	Treatment with H_2S	Composition			Age	Strength	Type of break	Remarks
		Furf. H_2S treated	Furf. NH_3 treated	HCl				
	hrs.	%	%	%	days	lbs/sqin		
47 a	2	70	10	20	3	400	Jaw	
b					19	500	Square	
c					21	950	Square	
d					23	700	Square	

e. The effect of aging on the tensile strength. In order to obtain a clearer picture of the relation between the tensile strength and the age of the test specimens, curves were drawn, using the age in days as the abscissae, and the tensile strength in pounds per square inch as the ordinates. These curves are presented on plates Nos. 1 to 14, inclusive. The number of the curve corresponds to "Run No." in Table No. 1.



Form E-5



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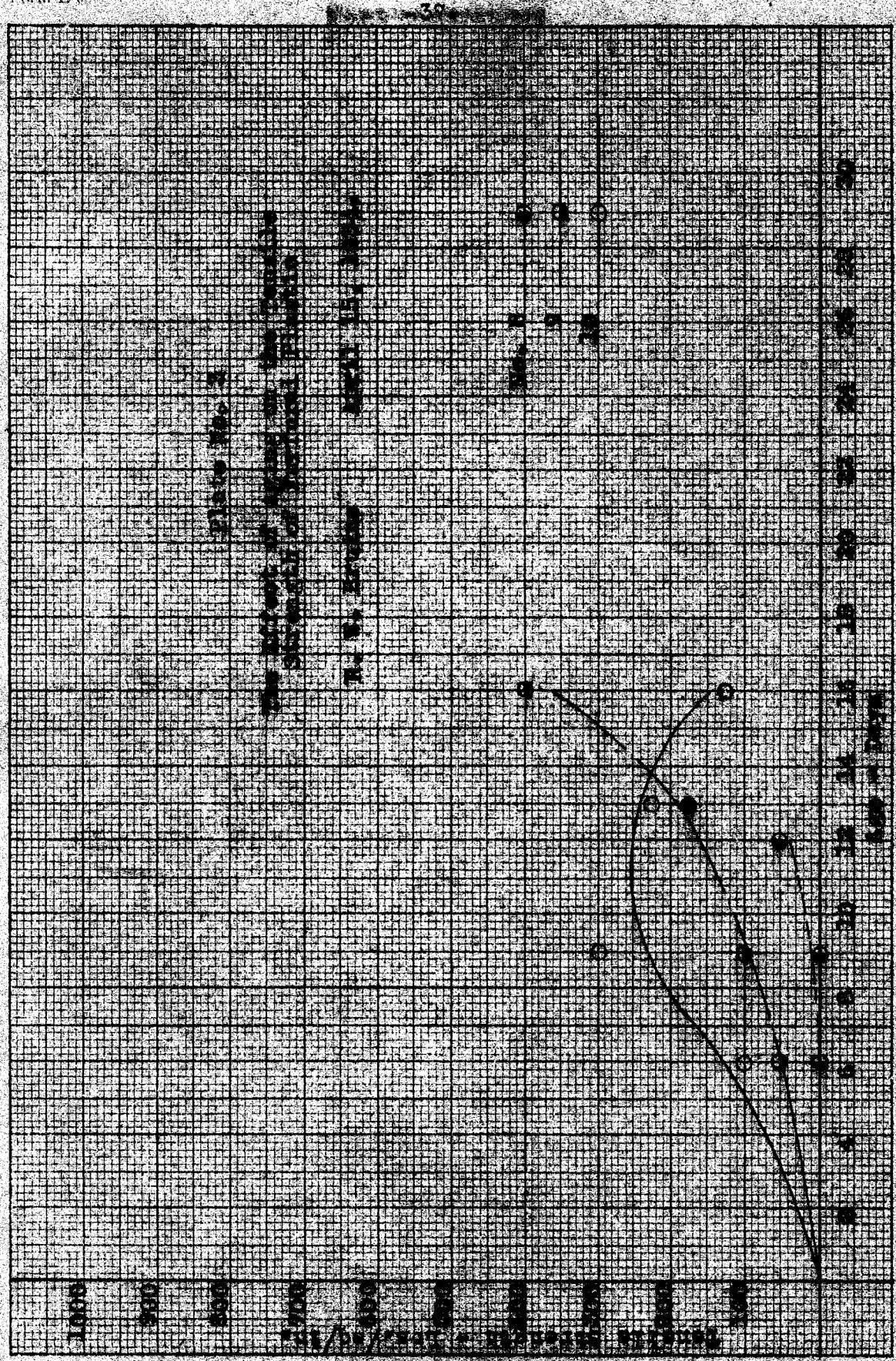

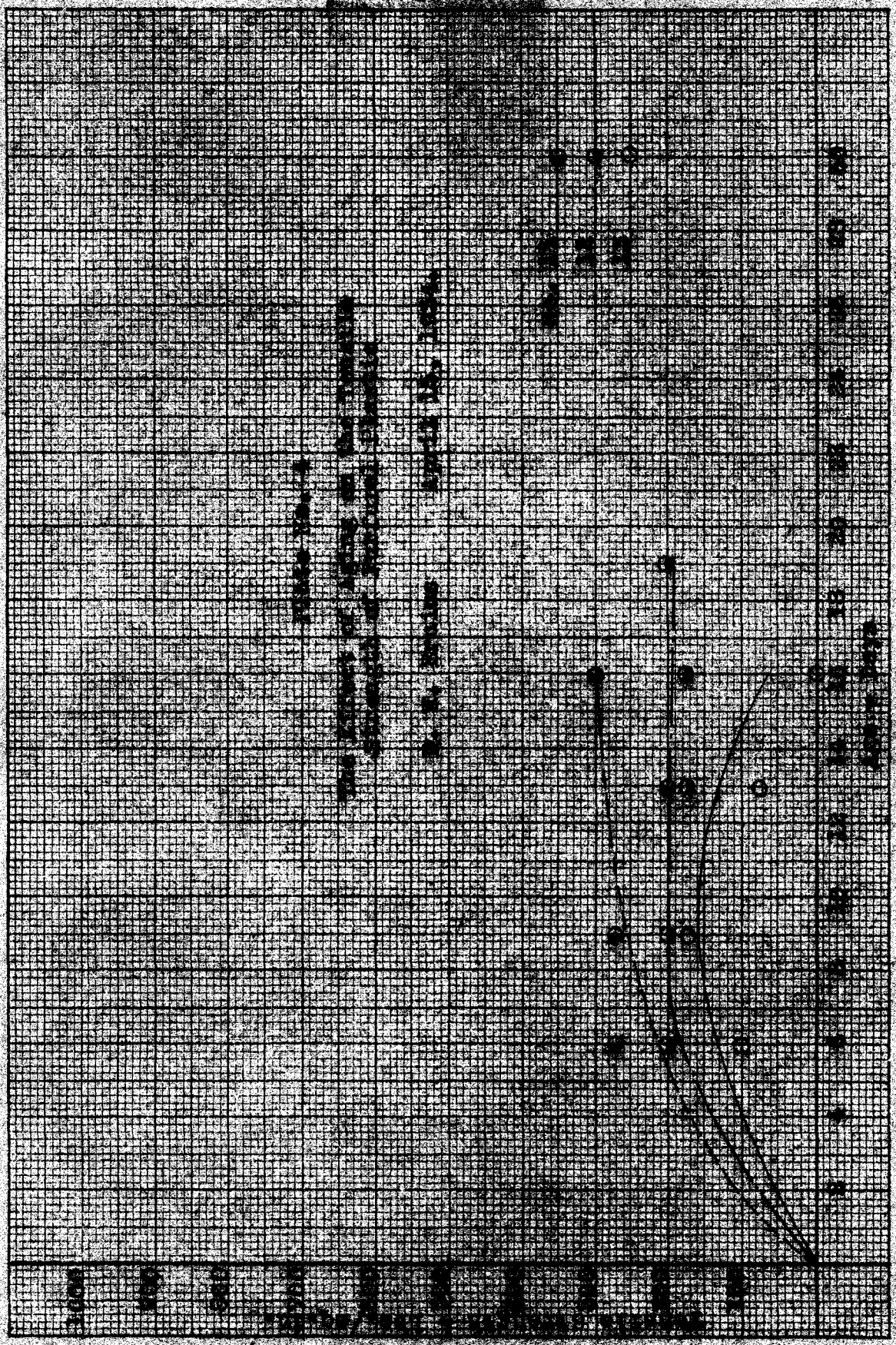

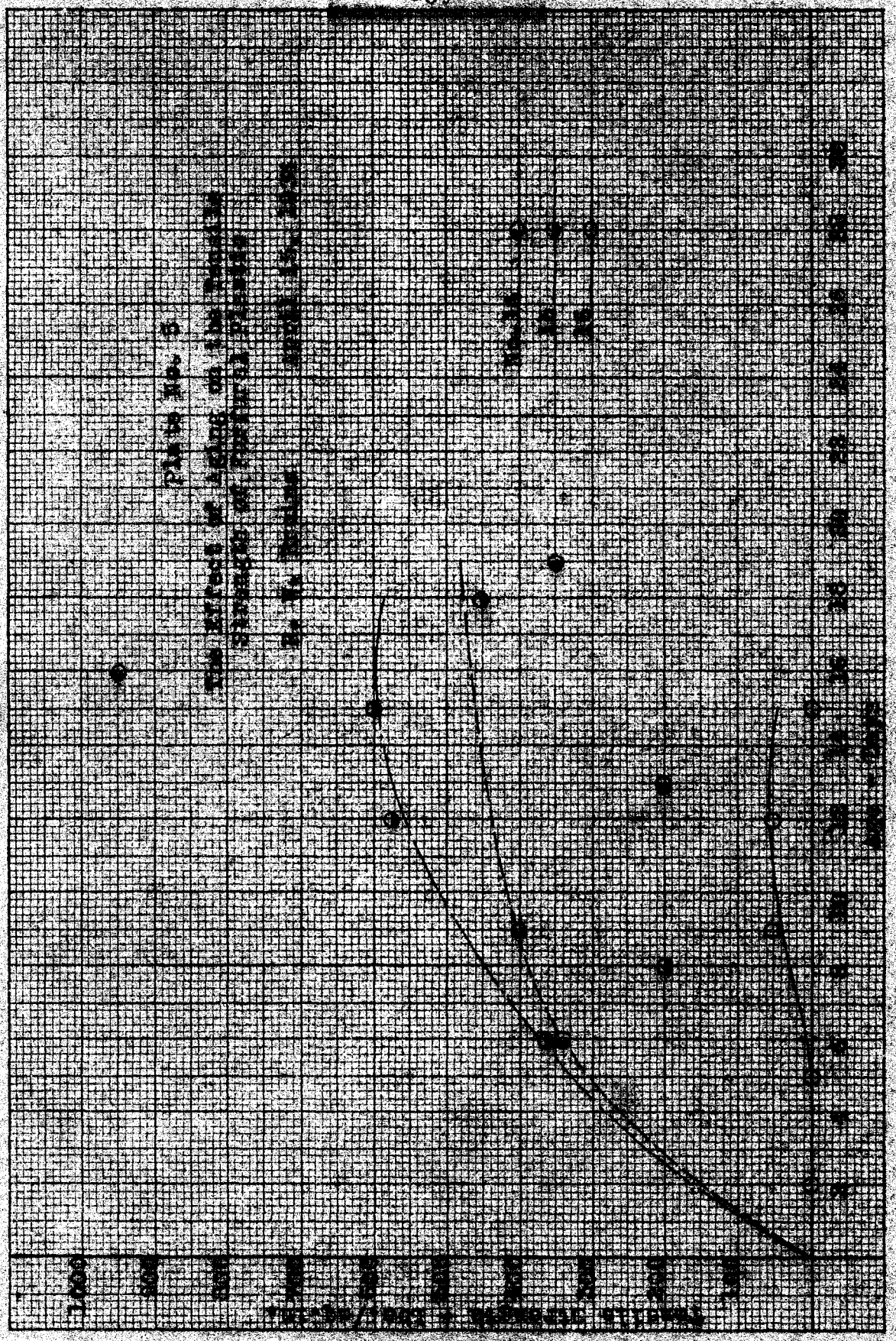

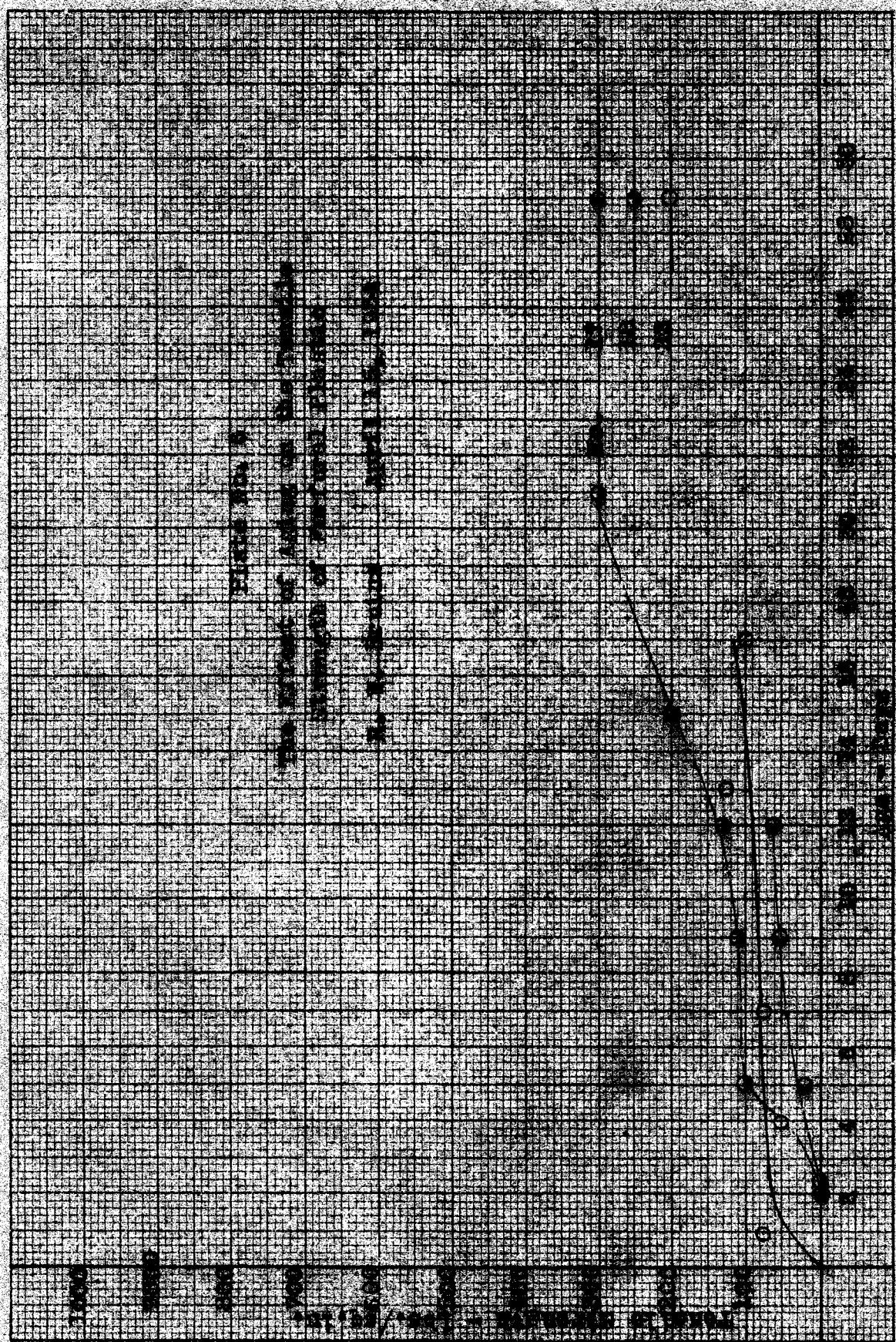

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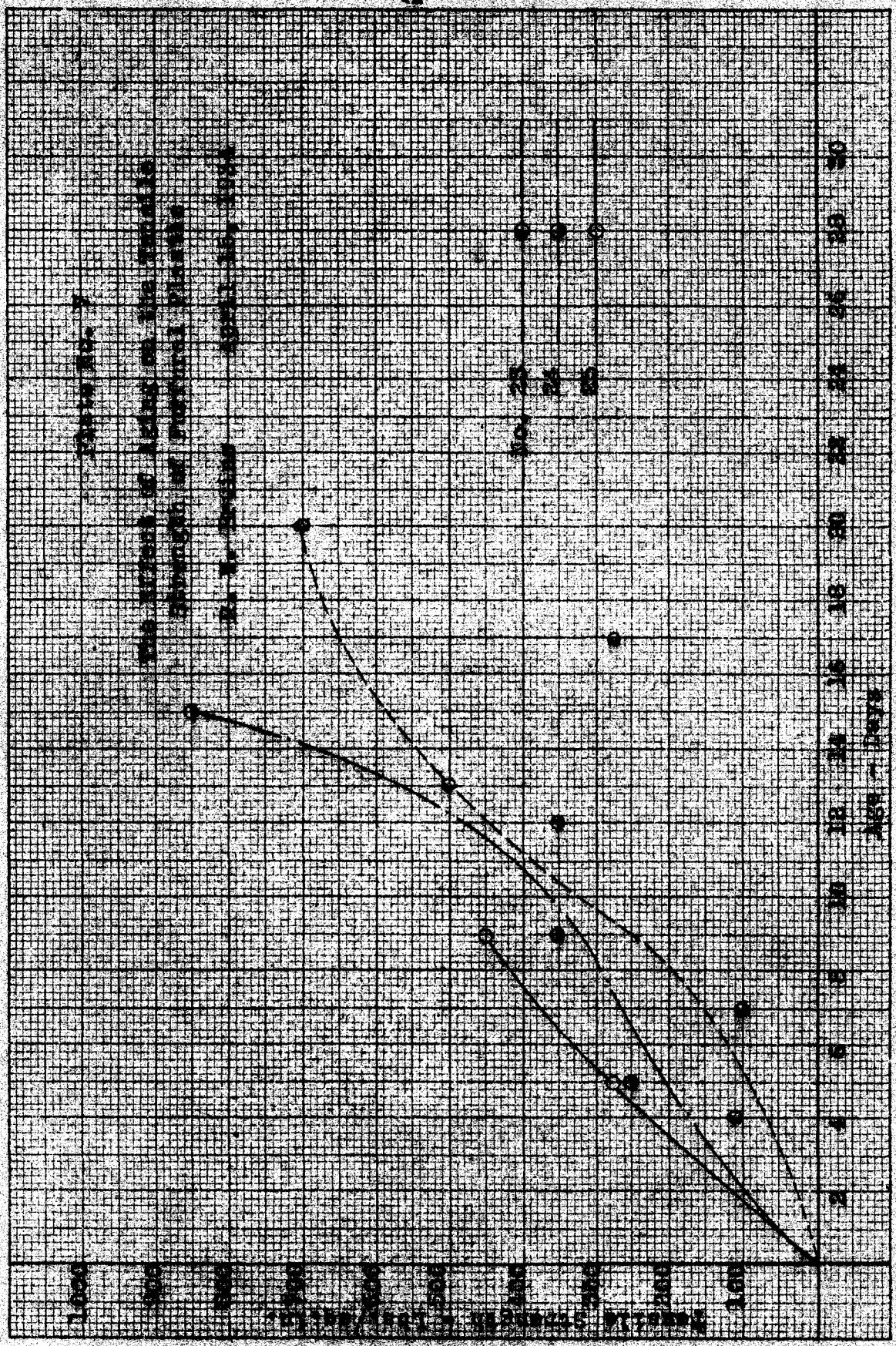
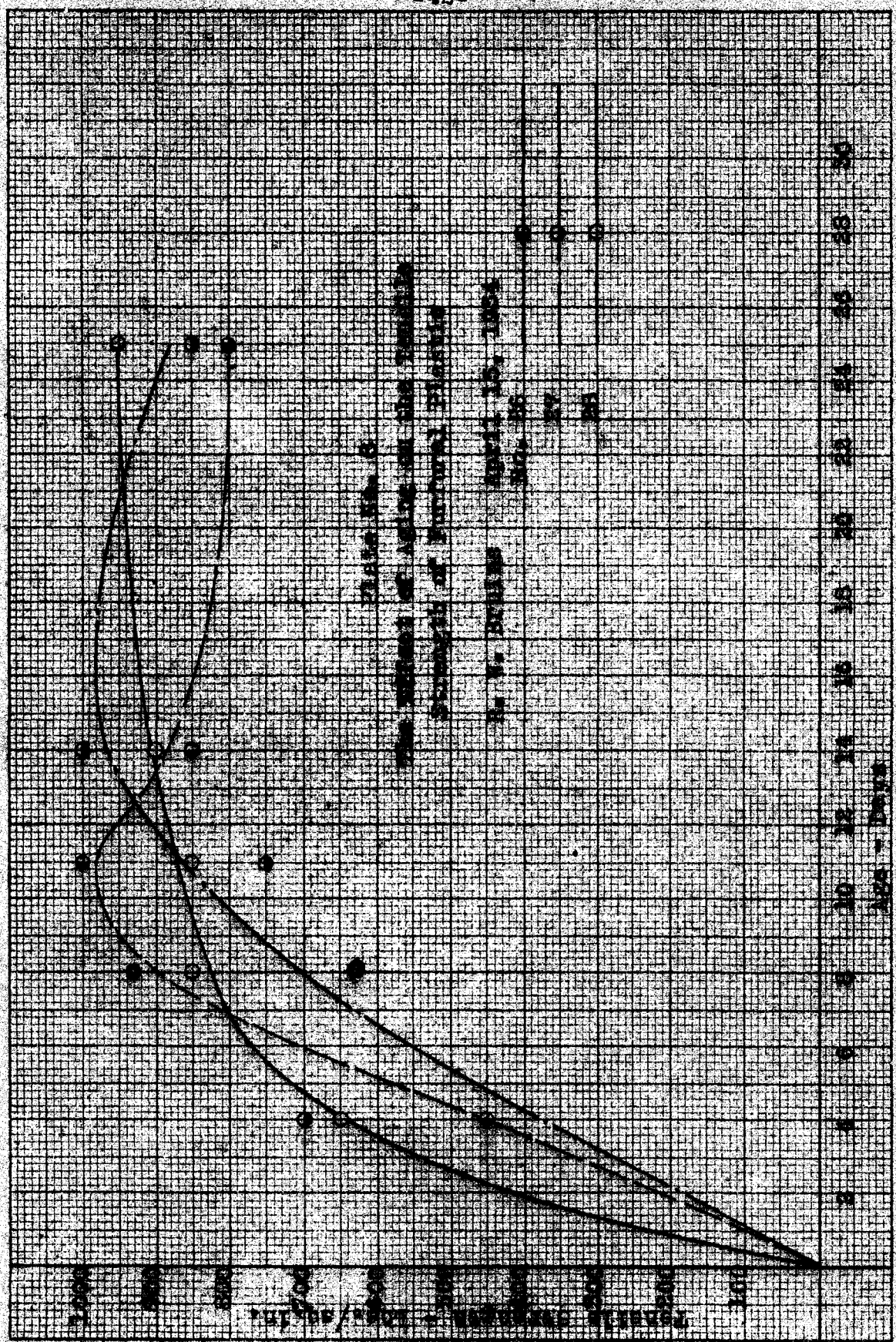
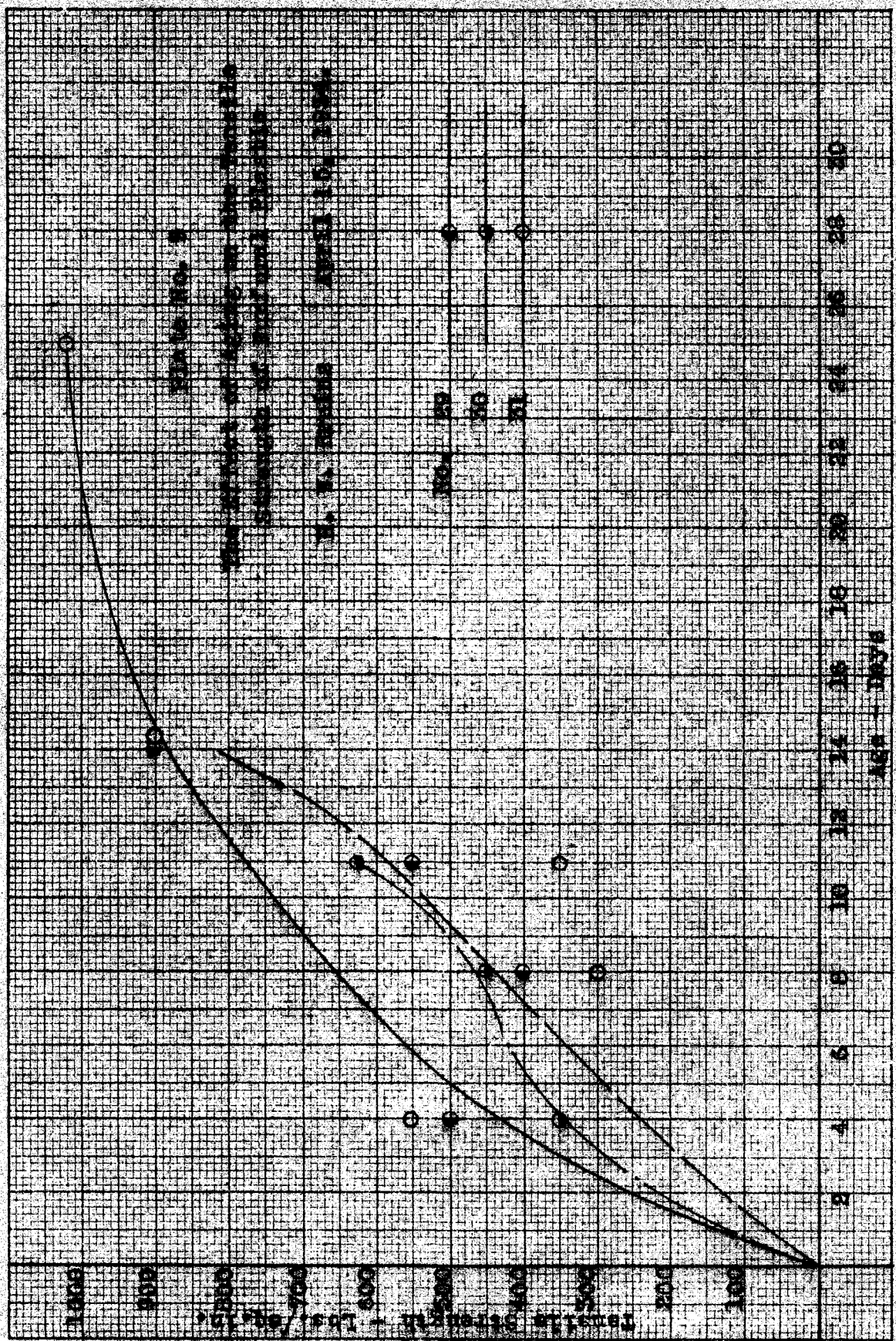
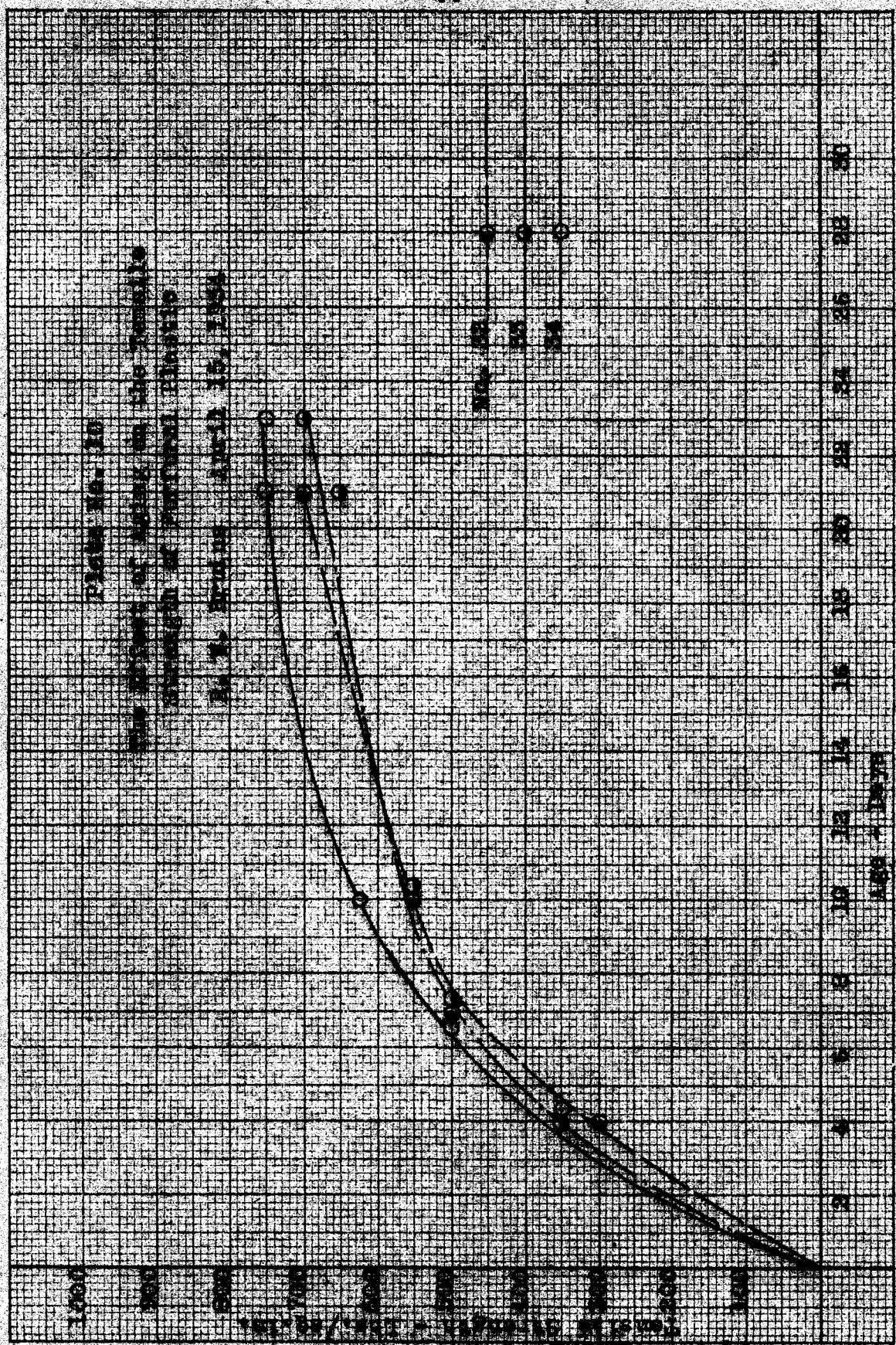
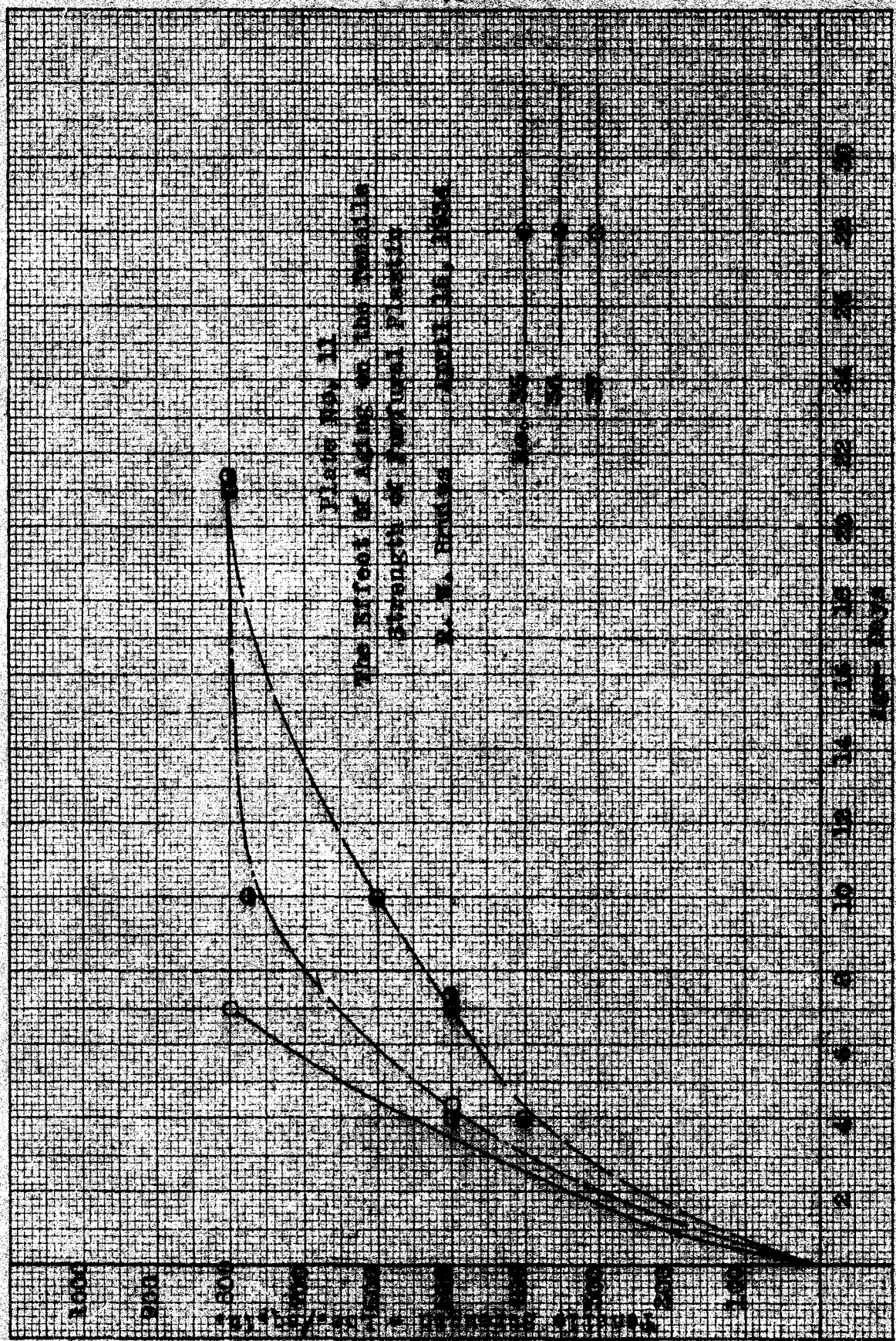
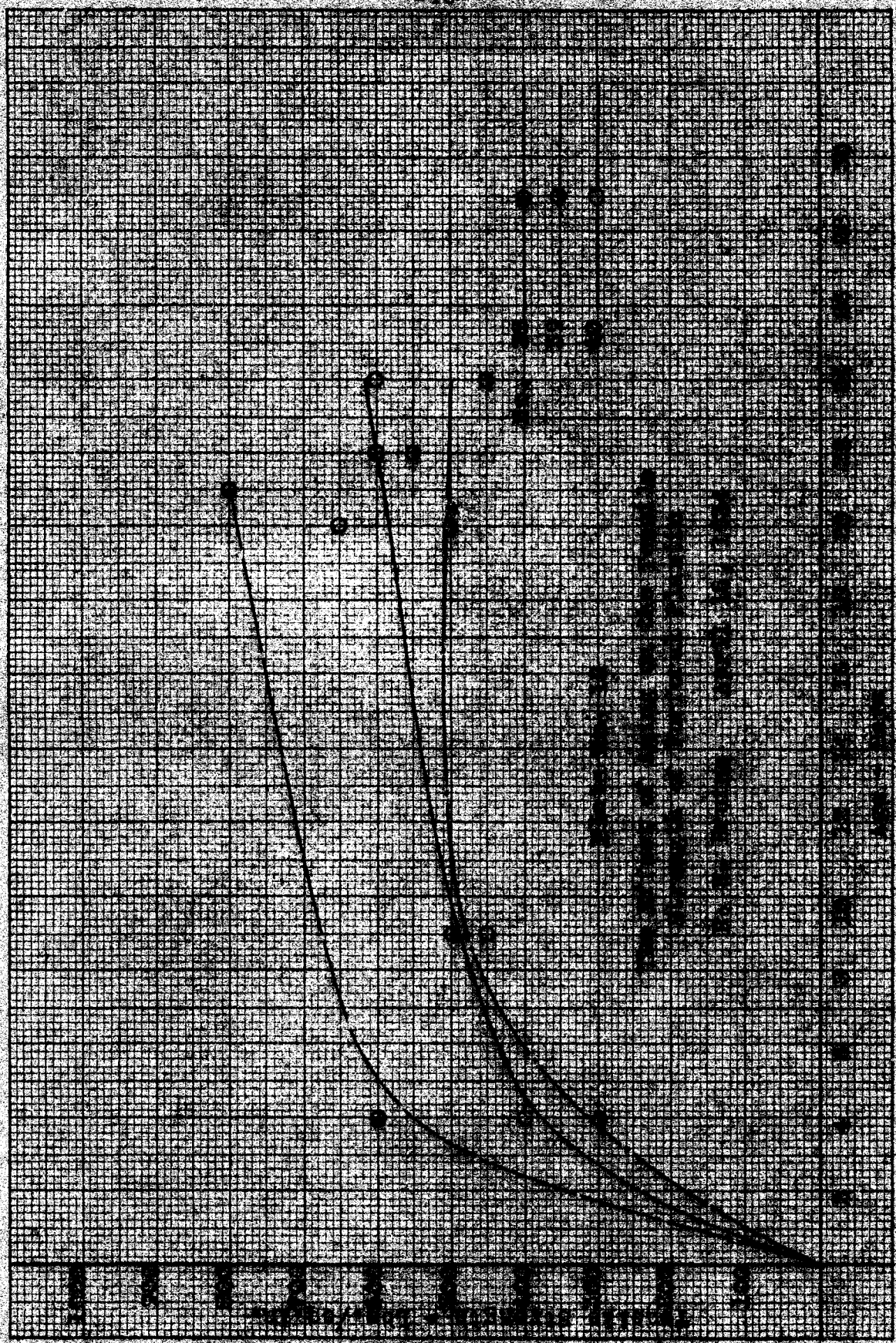


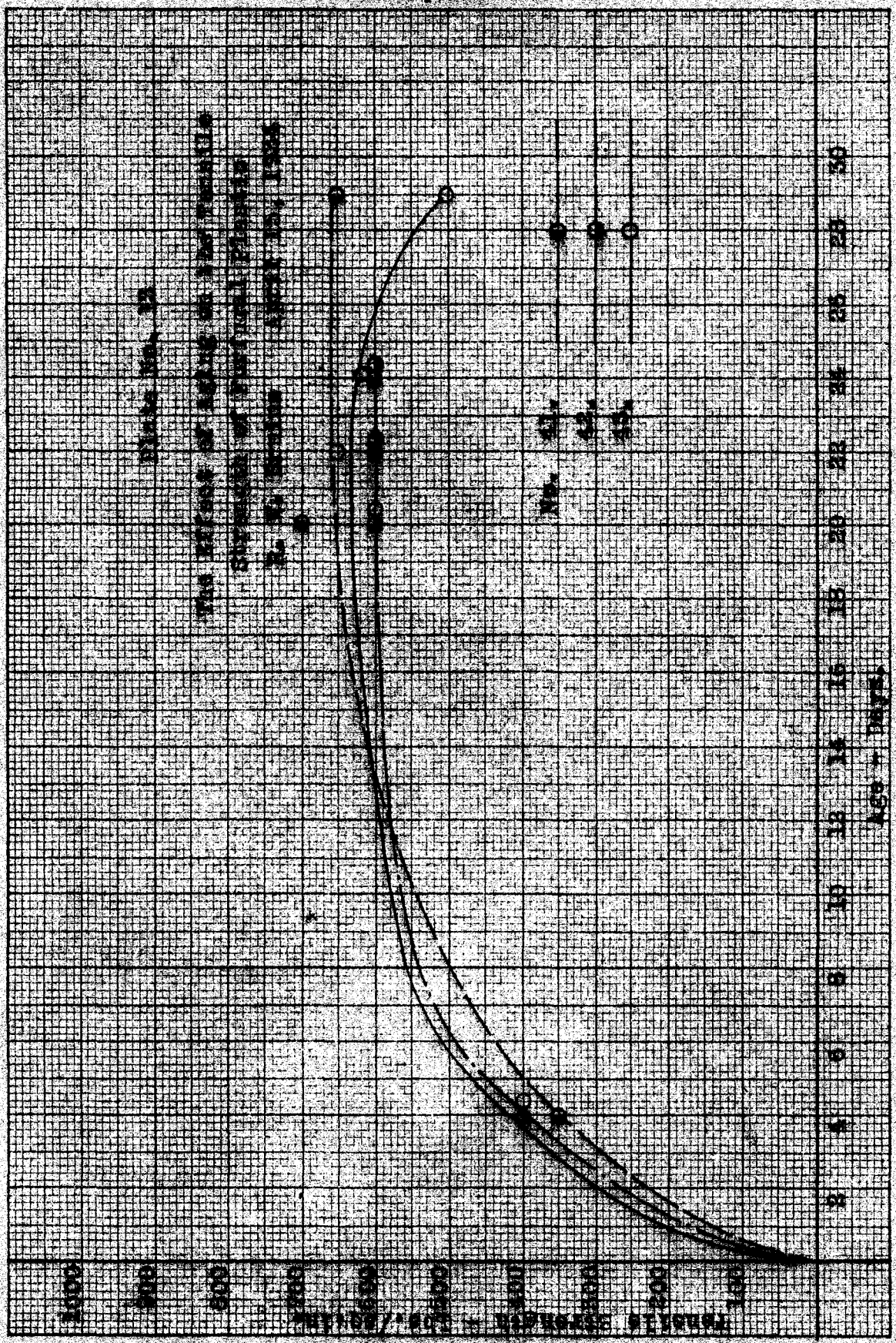


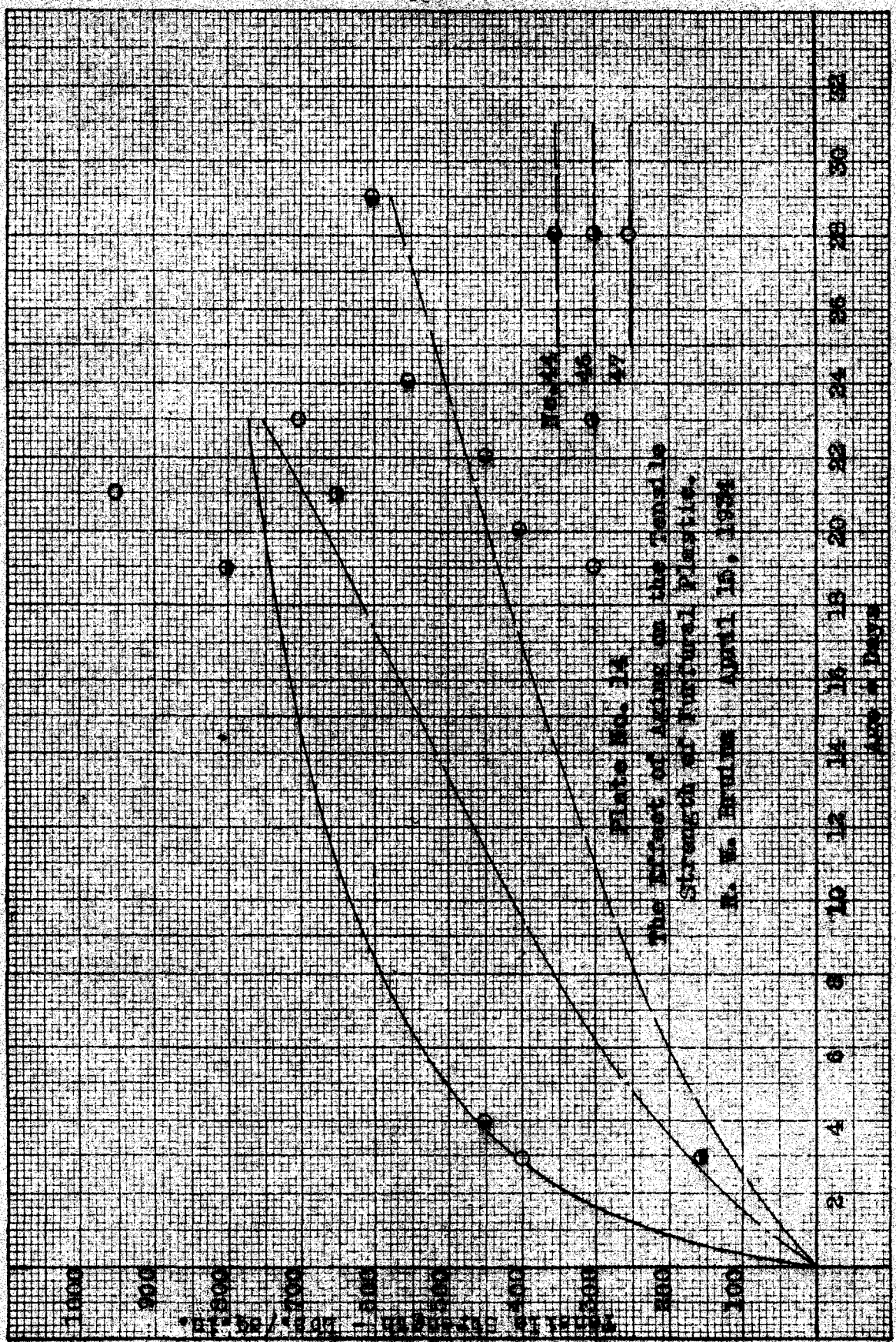





The Effect of Aging on the Ductility
and Strength of Lucite Plastics
Aging at 140°F.
Aging at Room Temperature






Stream and Plate Temperatures
at Various Points
April 19, 1956
Plate and Stream Temperatures
Plate and Stream Temperatures

1. Discussion. Curves Nos. 1 to 23, inclusive, relate to furfural plastic containing only furfural treated with hydrogen sulphide and hydrochloric acid. The curves show the change in the tensile strength of the plastic as its age increases.

Curves Nos 1 to 6 inclusive give the data on plastic resulting from the use of furfural treated with hydrogen sulphide for one hour. The curves show that a plastic having the best strength is produced by using hydrochloric acid and furfural treated with hydrogen sulphide for one hour in the ratio of 15 parts acid to 100 parts furfural, by volume. A maximum of 800 pounds per square inch tensile strength is attained at an age of about two weeks.

Curves Nos 7 to 12 inclusive relate to furfural plastic containing furfural treated with hydrogen sulphide for thirty minutes. An inspection of the curves will show that this amount of treatment with hydrogen sulphide is insufficient to produce a plastic having any appreciable strength. An acid concentration of 15% of the amount of the furfural used proved to be optimum, as in the case of treatment with hydrogen sulphide for an hour. The maximum strength of the plastics in this group was 400 pounds per square inch.

Curves Nos. 13 to 18 inclusive deal with plastics produced from furfural treated with hydrogen sulphide for two hours. In this group an acid concentration of from 10 to 15% was found optimum. The use of acid in excess of 25% of

the amount of furfural used (by volume) resulted in material that overheated when mixed, and in the event of hardening without being ruined by overheating, cracked within a short time after removal from the mold. For this reason no curves were drawn for Run Nos. 19, 20 or 21.

Curves Nos. 22 and 23 are drawn from data obtained by testing samples of plastic produced from furfural treated with hydrogen sulphide for three hours. In this case an acid concentration of 10% was found to be optimum. Apparently an increase in the amount of hydrogen sulphide treatment permits the use of less acid in the formation of a plastic.

Curves Nos. 24 to 47 show the effect of adding furfural treated with ammonia to the H_2S-furfural solution. Hydrochloric acid was used in the ratio of 20 parts to 100 parts of furfural, by volume.

Curves Nos 24 to 31 inclusive relate to furfural plastics containing furfurin solution, hydrochloric acid, and furfural treated with hydrogen sulphide for one hour. In this group tensile strengths exceeding 1000 pounds per square inch were obtained. The maximum strength is obtained when the material contains more furfurin solution than H_2S-furfural solution. A plastic containing 50% furfurin solution, 30% H_2S-furfural solution, and 20% hydrochloric acid was found the best.

Since previous tests showed that furfural treated with hydrogen sulphide for only half an hour did not produce satisfactory resins, no tests were made using this solution and

furfurin solution.

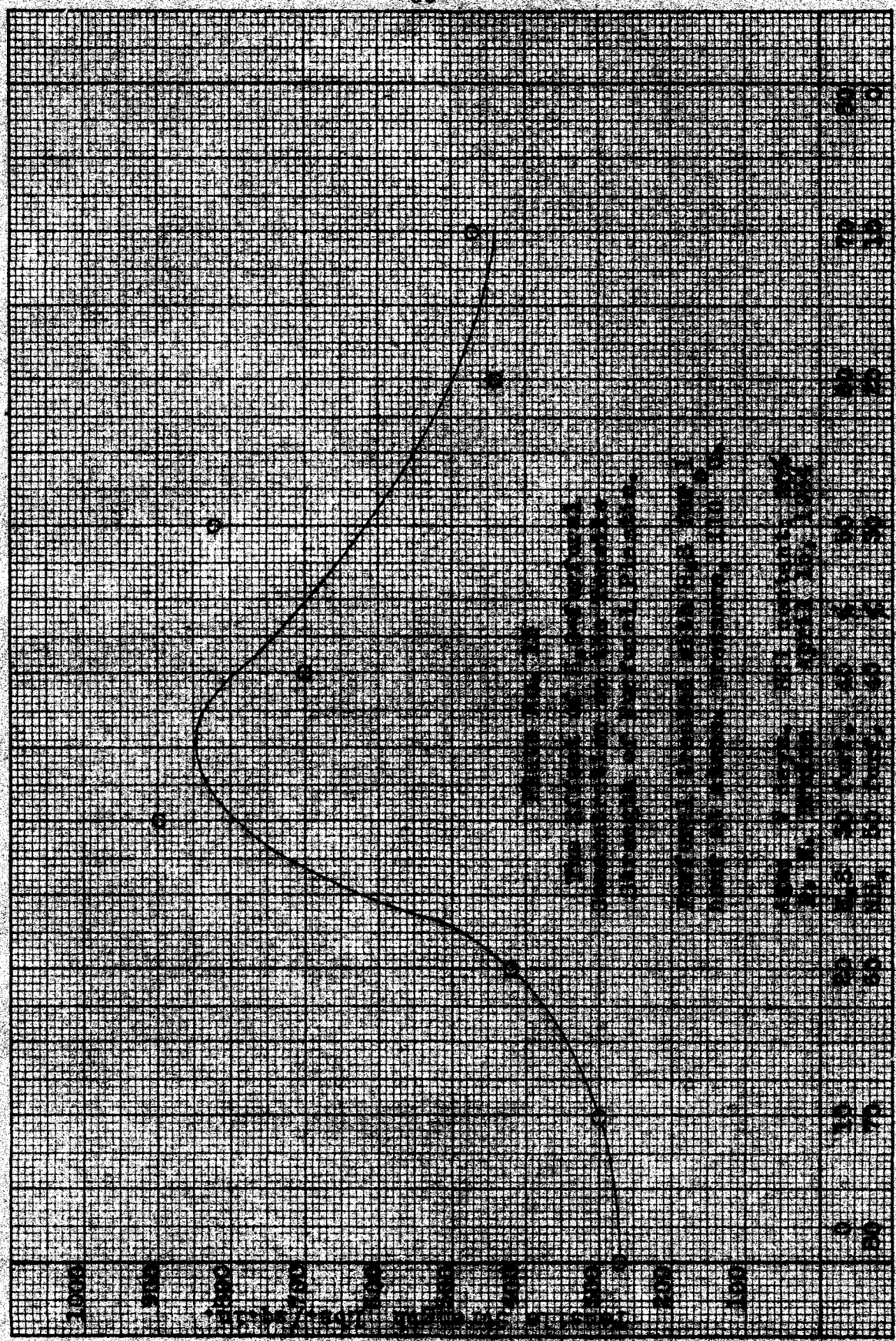
Curves Nos. 32 to 38 inclusive refer to plastics made from furfural treated with hydrogen sulphide for two hours. The tensile strength for this group is slightly lower than that of the previous group, the maximum for this group being 800 pounds per square inch. Best results were obtained by using 50% H_2S-furfural, 30% furfurin solution, and 20% hydrochloric acid.

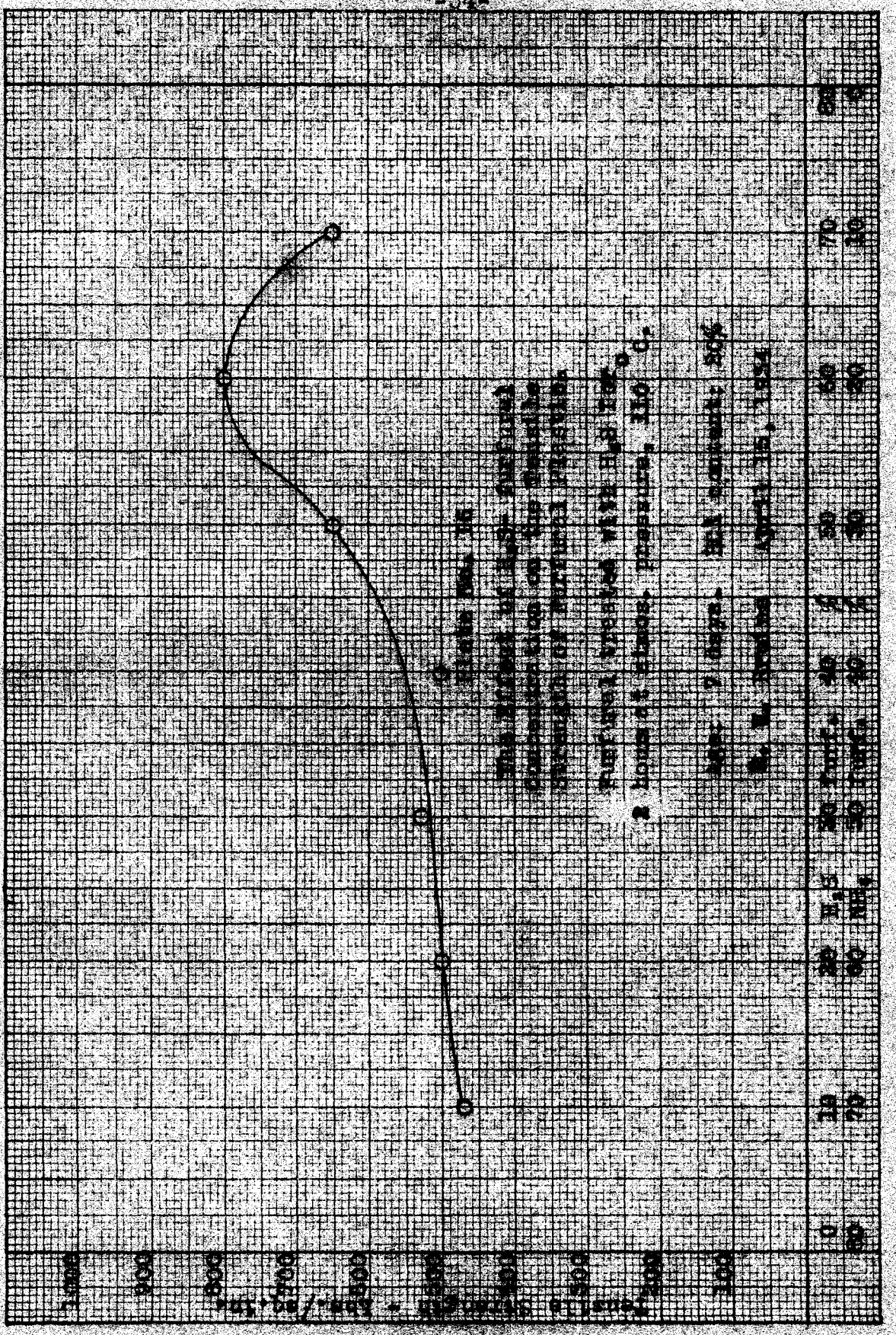
Curves Nos. 39 to 44 inclusive deal with plastic containing furfural treated with hydrogen sulphide for three hours. A further decrease in tensile strength is noted, the maximum for this group being 700 pounds per square inch. This strength was attained by a plastic containing 30% H_2S-furfural, 50% furfurin solution, and 20% hydrochloric acid.

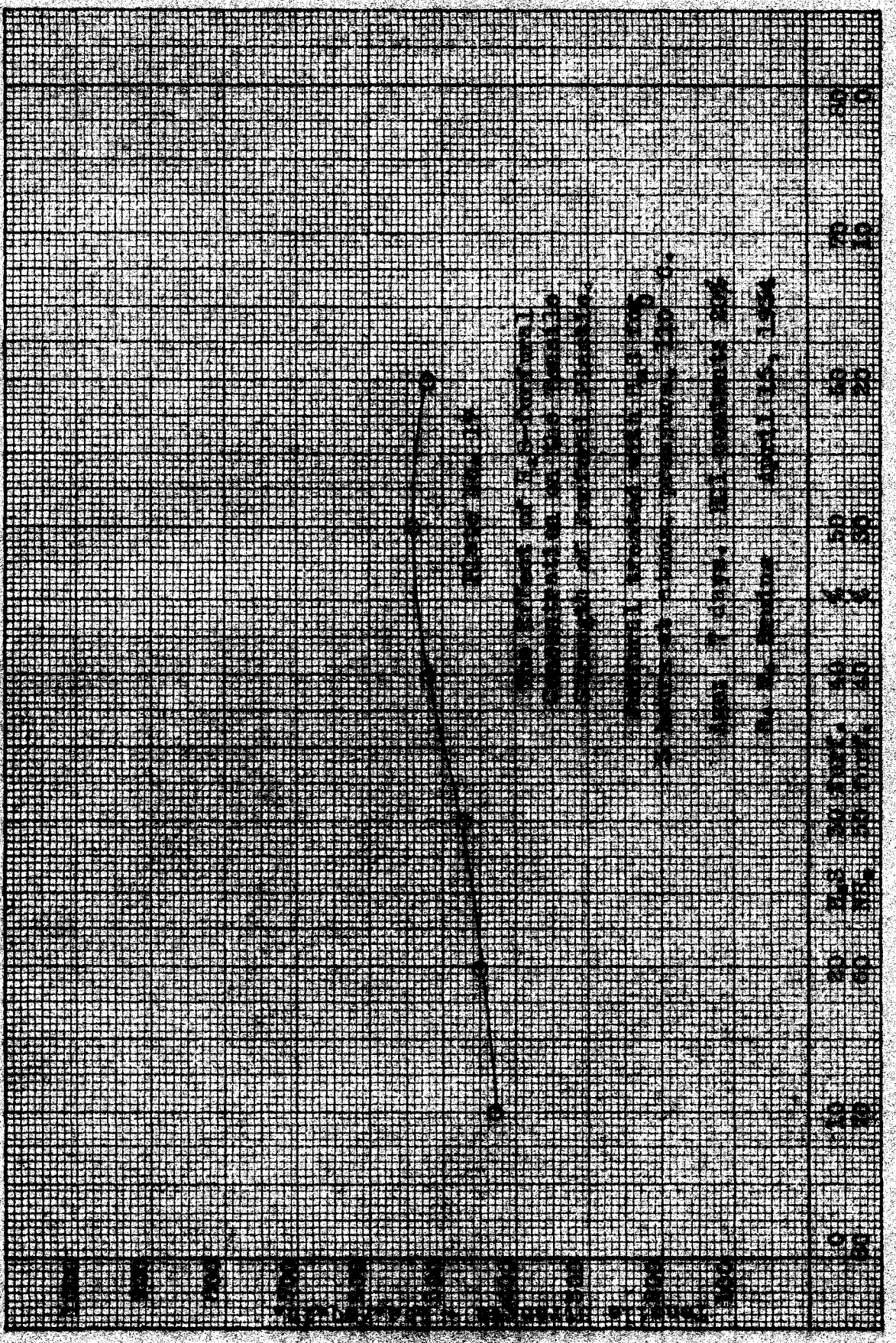
Curves Nos. 46 and 47 are duplicates of previous runs.

In using these curves it should be remembered that they are not intended to show exact tensile strength at any given time, but simply show the approximate change in strength as the specimens increase in age. In drawing the curves, no attempt was made to have them conform strictly to the points. Since each point is the result of only one test, it can not be taken as final conclusive evidence, particularly in view of the defects of the testing procedure used. More accurate results could be obtained by repeating these tests several times and getting an average of several specimens for each point on the curve.

f. The effect of the concentration of furfural treated with hydrogen sulphide on the tensile strength. A useful function of the curves showing the relation between tensile strength and age is to enable the obtaining of material for other curves. By selecting some definite age, a curve may be drawn showing the effect on the tensile strength of varying the concentration of the furfural treated with hydrogen sulphide in the plastic, or varying the composition. An arbitrary age of seven days was selected, and curves drawn using the percentage composition as abscissae, and the tensile strength in pounds per square inch, as taken from the proper age curve, as the ordinates. These curves are presented on plates Nos. 15 to 17, inclusive.





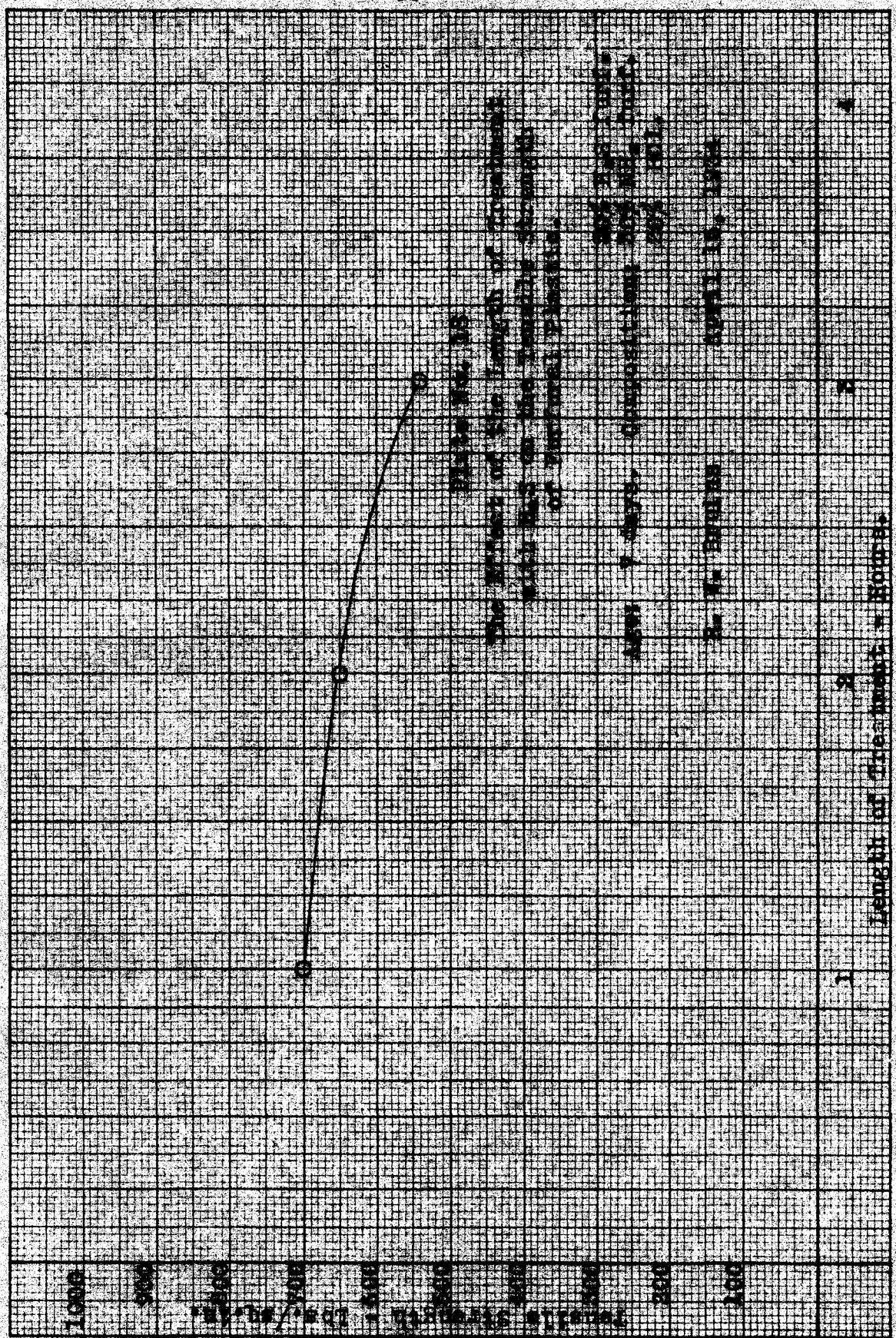


1. Discussion. The effect of varying the composition of furfural plastics formed by using various amounts of furfural treated with hydrogen sulphide for one hour, furfurin solution, and a fixed amount of hydrochloric acid is shown in plate No. 15. It is observed that a maximum strength is attained by the use of approximately equal parts of H_2S-furfural and furfurin solution. When furfural treated with hydrogen sulphide for two hours is used, the point of maximum strength shifts to the right (plate No. 16), to a percentage composition of 60% H_2S-furfural, 20% furfurin solution, and 20% hydrochloric acid. The highest strength attained using furfural treated with hydrogen sulphide for two hours was 800 pounds per square inch.

A fairly flat curve is obtained when furfural treated with hydrogen sulphide for three hours is used (plate No. 17). A maximum strength of 550 pounds per square inch is obtained when a mixture comprised of 50% H_2S-furfural, 30% furfurin solution, and 20% hydrochloric acid is used.

g. The effect of the length of treatment with hydrogen sulphide on the tensile strength. Three variables were taken into consideration in making up and testing the various specimens. These variables were (1) age; (2) composition; and (3) the time of treatment with hydrogen sulphide. The effects of age and composition have been presented. A curve showing the effect on the tensile strength of varying the time of treatment with hydrogen sulphide is presented as plate No. 18. The strength in pounds per square inch is plotted as the ordinates, and time of treatment with hydrogen sulphide, in hours, as the abscissae.

This curve is taken from data on representative samples, seven days old, and having a composition of 50% H_2S-furfural, 30% furfurin solution, and 20% hydrochloric acid.



1. Discussion. Plate No. 18 presents a curve which shows the effect of incorporating furfural treated for various lengths of time with hydrogen sulphide on the tensile strength of furfural plastic. The downward slope of the curve indicates that an increase in the time of treatment with hydrogen sulphide decreases the tensile strength of the resulting plastic. The minimum length of time, however, that furfural should be treated with hydrogen sulphide is one hour. Tests have shown that inferior material is produced when shorter periods of treatment with hydrogen sulphide are maintained.

B. The use of polymerizing agents other than hydrochloric and sulphuric acid.

1. Defects of acid polymerizing agents.

From the beginning of the work on furfural plastics, it has been observed that hydrochloric and sulphuric acids had unusual ability to cause polymerization of furfural or its derivatives. The use of these acids is attended, however, by numerous difficulties. The first of these is shrinking, one of the first defects of the plastic that was observed. The large amount of shrinking also causes cracking and warping when the plastic is formed into sections of any size. Beside these difficulties, the acid remaining in the plastic after reaction is complete makes the material very acidic, causing iron articles in its vicinity to rust, and deterioration of cloth and paper near it. The acidity is very difficult to remove, either by solvents, or by placing the specimens in contact with bases such as caustic or gaseous ammonia. Best results are obtained by baking, but this process is somewhat limited by the size of the article.

Because of these numerous difficulties resulting from the use of acidic polymerizing agents, several attempts have been made to find other polymerizing agents which would cause the liquid material to solidify, and still not have injurious after effects. Previous investigations (6) attempted the solution of this problem by the addition of one percent of various metallic salts, as suggested by Trickey and Miner (51)

to be of benefit in the catalytic reactions of furfural. None of these salts resulted in the formation of a solid material.

While it was evident from a study of these investigations that metallic salts in themselves are ineffective, it was thought that their use in conjunction with the acid would produce beneficial results, such as reducing the amount of acid required or helping to eliminate shrinking or cracking.

2. Method of procedure.

As a means of determining the effect of various compounds on the plastic, one gram of the compound was mixed with ten cubic centimeters of concentrated hydrochloric acid, and then poured into thirty five cubic centimeters of furfurin solution. The liquid was poured into tubes, and after setting was pushed out of the tubes. One gram of compound is equivalent to about two percent by weight of the compound in the final mixture.

a. Presentation of data. The effect of the various compounds on the furfurin-furfural plastic is presented in Table 2.

TABLE NO. 2

Catalytic effects of various compounds on the furfurin-furfural plastic.

Compound	Results
Phthalimide	Sample cracked.
Potassium chromate	Sample cracked.
Sodium tungstate	Set rapidly, cracked.
Casein	Sample cracked.
Potassium chlorate	Sample cracked.
Gallic acid	Set rapidly, cracked.
Oxalic acid	Sample cracked.
Pyridine	Failed to set.
Formic acid	Sample cracked.
Aldehyde-ammonia	Sample cracked.
Manganese dioxide	Sample cracked.
Potassium permanganate	Evolved chlorine, cracked.
Ferrous ammonium sulphate	Very little checking.
Sodium acetate	Sample cracked.
Cobalt nitrate	Sample cracked.
Sodium dichromate	Slight cracking.
Potassium ferricyanide	Sample cracked.
Molybdic acid	Slight cracking.
Sulphur	Sample cracked.
Sodium dichromate	Slight cracking.
Potassium iodide	Sample cracked.

1. Discussion. The most beneficial results were obtained with the use of ferrous ammonium sulphate. To make a more complete test of this compound, a larger article was molded, a cube two inches on a side. This cube cracked after several days. Evidently ferrous ammonium sulphate, while beneficial, is not sufficiently so to prevent cracking except in rather small pieces.

b. Use of metallic chlorides. In addition to the compounds mentioned in Table 2, a number of metallic chlorides were tried. The chloride was selected since hydrochloric acid was used in conjunction with the metallic salt. In Table No. 3 is presented a list of metallic chlorides added to the plastic, together with the results obtained. The amount of chloride added was .5% of the weight of the plastic. The samples after setting were removed from the molds, and coated with paraffin. The paraffin was removed after two days, and the blocks were inspected on the third day to see if they had developed cracks.

TABLE NO. 3

The catalytic action of metallic chlorides on the furfurin-furfural plastic.

Chloride	Result
Ferrous chloride	Cracked
Bismuth chloride	Cracked
Mercuric chloride	Cracked
Chromic chloride	Cracked
Cobalt chloride	Cracked
Magnesium chloride	Cracked
Lead chloride	Cracked
Strontium chloride	Cracked
Stannous chloride	Cracked
Cupric chloride	Cracked
Manganous chloride	Slight cracking.
Cadmium chloride	Cracked
Cuprous chloride	Cracked
Barium chloride	Cracked
Ammonium chloride	No cracking.
Mercurous chloride	Cracked
Potassium chloride	Cracked
Zinc chloride	Cracked
Sodium chloride	Cracked
Nickel chloride	Cracked

1. Discussion. The best results were obtained with the use of ammonium chloride. A number of larger pieces made with the addition of this salt revealed, however, that ammonium chloride is not effective in preventing the cracking of large pieces.

c. The use of silicon tetrachloride. The use of silicon tetrachloride resulted in the formation of a plastic mass without the addition of any hydrochloric acid. This chloride was found capable of polymerizing either pure furfural or furfural treated with ammonia or oxygen. Considerable heat was developed when the chloride was added to the furfural, which necessitated cooling the mixture in a water bath. Silicon tetrachloride in the amount of eight percent by volume of the total mixture was found to be sufficient to cause polymerization with the final formation of a hard mass. The final product resembles black glass, as it is very hard and shiny, but is quite brittle. The resin is somewhat acidic, though not so much so as the plastic formed by the use of hydrochloric acid.

d. The action of the silent electric discharge. A previous investigation had been made of the polymerizing action of the silent electric discharge (8). The result obtained in this investigation was not thought to be conclusive, as the furfural was put into a glass container placed between plates at a potential difference of 50,000 volts. The glass container possibly acted to insulate the furfural from the

action of the discharge. An apparatus was constructed to permit discharge directly through the furfural. This apparatus was a large diameter glass tube, with a metal plate at the bottom closed end. The other end of the tube was fitted with a cork, through which a rod with a second plate attached could be moved. In this way the distance between the plates could be varied. The tube was filled with furfurin solution, and a potential difference of 10,000 volts imposed on the plates by means of a transformer. No polymerization of the furfural was observed, regardless of the distance between the plates. The furfurin solution was treated for half an hour with no result other than a slight rise in temperature.

A small amount of hydrochloric acid was added to start the reaction, and the voltage imposed once more. After fifteen minutes of treatment no change in the viscosity of the solution could be noted.

C. The determination of furfurin content of furfurin in furfural solutions by means of specific gravity.

In the treatment of furfural with ammonia to obtain the furfurin-furfural solution, some method of determining the amount of furfurin formed is essential, in order to obtain a solution of the proper furfurin concentration. Several methods are available for this determination.

1. Available methods.

a. Gain in weight. The most obvious method is to weigh the furfural before and after treatment with ammonia. In order to prevent loss of water vapor, the flask must be fitted with a reflux condenser. Since the furfural absorbs the ammonia very rapidly, no ammonia is lost if the gas is bubbled through the liquid. This gravimetric method, while simple, requires a reflux condenser to prevent loss, and is limited to the treatment of small quantities.

The Kjeldahl method for nitrogen does not give quantitative results when applied to the analysis of furfurin-furfural solutions (1).

b. Use of flow meters. A second method is to measure the amount of ammonia passed into the solution. This can easily be done by inserting some form of flow meter, such as an orifice equipped with a manometer, into the ammonia line. By holding the flow constant, the amount of ammonia desired can be obtained by treating for a corresponding length of time.

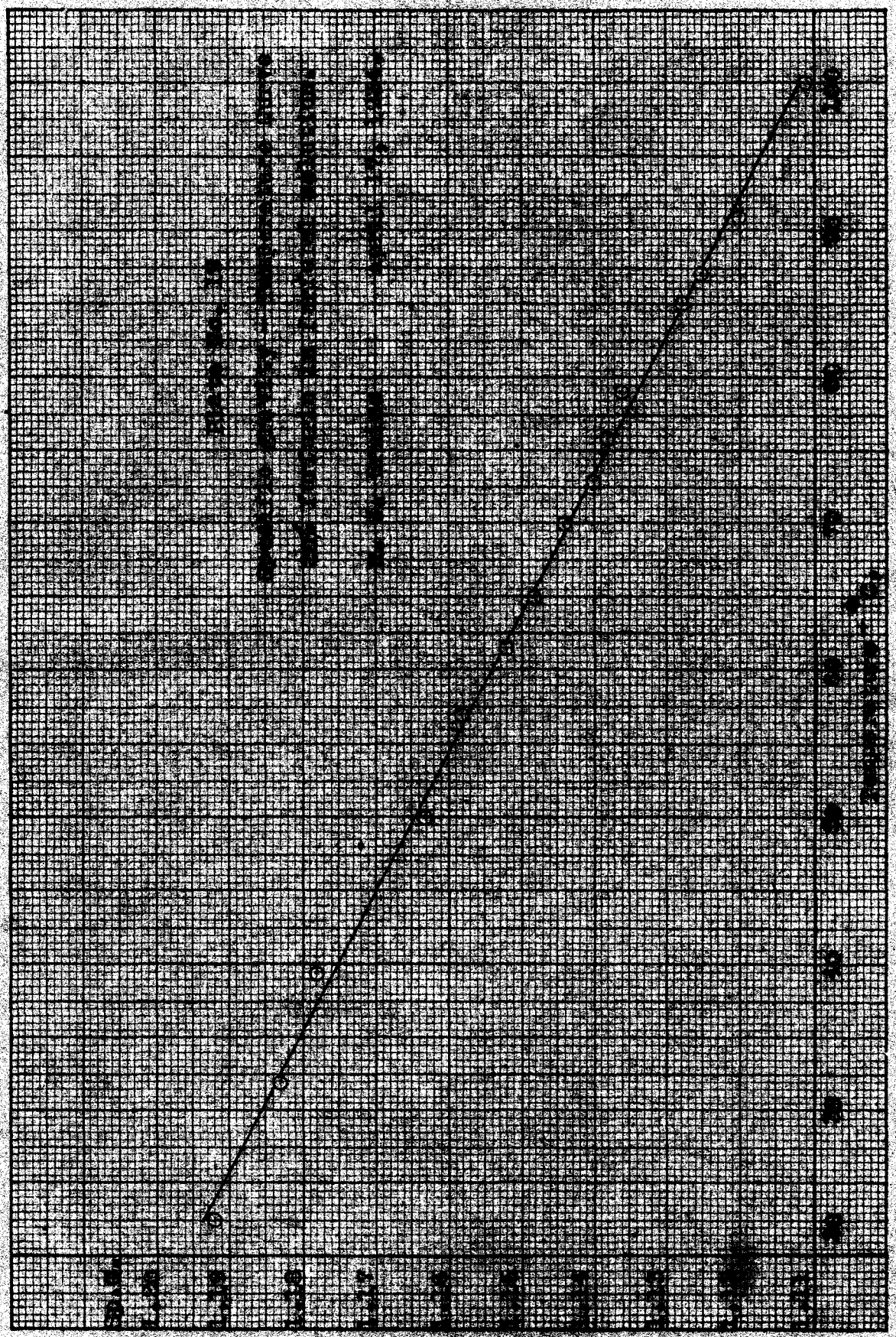
c. The gain in specific gravity. A third method, which is very simple, and can be applied to the treatment of any amount of furfural, is to determine the specific gravity of the solution. It has been found that the addition of ammonia to furfural raises the specific gravity of the resultant solution sufficiently to enable the determination of the furfurin content by the change in specific gravity. The specific gravity varies, of course, with the temperature, so that the temperature of the solution must be known in order to determine the furfurin content by this method.

1. Presentation of data. The specific gravity of a 20% solution of furfurin in furfural was obtained at various temperatures. These data are presented in table No. 4. A graphical presentation is found in plate No. 19. It will be observed that the specific gravity of the solution varies inversely as the temperature, and is a straight line function. In the procedure of treating furfural with ammonia, the liquid must be kept hot. In order to determine when sufficient ammonia has been passed into the furfural, the temperature of the solution is obtained, and the corresponding specific gravity read from the curve. When the specific gravity of the solution corresponds to the value taken from the curve, a 20% solution has been obtained.

TABLE NO. 4.

The Relation between the Temperature and Specific Gravity of a 20% Solution of Furfurin in Furfural.

Temperature °C.	Specific Gravity
22.5	1.192
32.0	1.184
39.5	1.178
50.0	1.163
57.0	1.158
61.5	1.152
65.0	1.148
70.0	1.144
73.0	1.140
76.0	1.138
79.0	1.136
85.0	1.128
87.0	1.125
91.0	1.120
100.0	1.111



D. The use of plasticizing agents.

The formulae of most plastic materials include a compound usually referred to as a "plasticizing agent." These compounds are substances which increase the workability of the plastic, reduce cracking, and permit the plastic to be formed into somewhat complicated shapes. The classical example of a plasticizer is the use of camphor as a plasticizing agent for nitro cellulose, the resultant material being the well known and much used molding compound known as celluloid, or pyroxylin.

1. The necessity for plasticizing agents.

The furfurin-furfural plastic has several defects. The most troublesome of these is shrinking and warping, which frequently occur to the extent of producing cracking. One of the functions of a plasticizing agent is to prevent warping and shrinking, hence several substances were added to the furfurin-furfural plastic in the hope of producing beneficial effects such as are obtained when camphor is added to nitro cellulose.

2. The use of dibutyl phthalate.

One of the most widely used plasticizers, for nitro cellulose molding materials in particular, is dibutyl phthalate. A quantity of this material was obtained through the courtesy of the Commercial Solvents Corporation, and tested for its ability to plasticize the furfurin-furfural compound.

a. Direct addition. The first attempt to use the dibutyl phthalate was made by mixing a small quantity of the oily liquid into the hydrochloric acid-furfurin-furfural mixture. Owing to the immiscibility of the dibutyl phthalate, the liquid separated, and rose to the top. The solid resin in the bottom of the mold was covered with an oily liquid, the volume of which was approximately the combined volume of the dibutyl phthalate and acid added. The resin in the bottom of the mold was quite hard, and unusually resilient, however it cracked after exposure to the air for a few days. It was evident that the direct addition of the dibutyl phthalate to the furfurin-furfural plastic would not be satisfactory.

b. Alcoholic hydrochloric acid. The source of the trouble in this first attempt was the immiscibility of aqueous hydrochloric acid and dibutyl phthalate. To obviate this difficulty, instead of using aqueous hydrochloric acid, a quantity of butyl alcohol was treated with anhydrous hydrochloric acid gas, thus forming alcoholic hydrochloric acid. It was found that this solution and dibutyl phthalate were miscible in all proportions. In the production of resins using the acid alcohol no difficulty was experienced by the dibutyl phthalate separating out. A series of test blocks was made, using various quantities of dibutyl phthalate in an attempt to find the optimum amount, and to find the minimum amount required to prevent cracking. Of these samples, the

block containing 50 cubic centimeters of furfurin-furfural solution, 20 cubic centimeters of alcoholic hydrochloric acid, and 15 cubic centimeters of dibutyl phthalate was found to be the best. The resins were quite hard, shiny, did not crack on exposure to air, and due to the alcohol content, had a pleasant odor. An unusual feature of the resin was its very low specific gravity, only 1.05. The cause for this low value may be the large alcohol content.

The use of alcoholic solutions of hydrochloric acid requires an additional step in the production of furfurin-furfural plastics, that is, the preparation of the alcoholic acid. Since a procedure that would eliminate this extra step would be of value, some method that would permit the use of aqueous hydrochloric acid was sought. It was thought that possibly enough butyl alcohol could be added to keep aqueous hydrochloric acid and dibutyl phthalate from separating. This idea was tested by making a series of samples, each having the same furfurin-furfural solution, dibutyl phthalate, and acid content, but varying amounts of butyl alcohol. The samples containing below 10 cubic centimeters of alcohol per 50 cubic centimeters of furfurin solution suffered from the separation of the dibutyl phthalate. No separation of the plasticizer, or cracking of the test piece, was observed in the samples containing larger amount of alcohol, however due to the diluting action of the alcohol, the specimens were too soft to be of value. This series of tests indicated that

butyl alcohol would be unsatisfactory as a blending agent for aqueous hydrochloric acid and dibutyl phthalate.

Since beneficial results were obtained by the use of alcoholic hydrochloric acid and dibutyl phthalate, there was the possibility that the alcoholic acid used alone would have some improved action. Test samples prepared using the acid alcohol without the addition of dibutyl phthalate were found to be without merit. The specimens cracked within a few hours after removal from the mold. This test was evidence of the fact that the value of the alcoholic hydrochloric acid was not due to a plasticizing action of the acid solution itself, but to the ability of the alcohol of forming a homogeneous mixture of dibutyl phthalate and the furfurin-furfural solution.

c. The use of sulphuric acid. These tests showed that an acid containing water prevented the uniform distribution of dibutyl phthalate. In the case of hydrochloric acid, the addition of water was avoided by the use of alcohol. Since concentrated sulphuric acid is practically 100% H_2SO_4, the use of this acid would add very little, if any, water, and hence should permit the use of dibutyl phthalate without the addition of alcohol. As a test of this theory, a test block made up of furfurin-furfural solution, dibutyl phthalate and sufficient sulphuric acid to cause polymerization was molded. The result failed to agree with theory, as the dibutyl phthalate separated out. The addition of a small amount of butyl alcohol

to the mixture prevented the separation, however, and some excellent samples were prepared. The resins formed were hard, glossy, and had very little shrinkage.

3. The use of glycerine and other plasticizers.

Glycerine is used as a plasticizer for several plastics, among them "Catalin," a phenol-formaldehyde condensation product. Test samples made up using aqueous hydrochloric acid, furfurin-furfural solution and glycerine were disappointing, as the resin formed was soft and somewhat porous. Other compounds on the order of glycerine tested were methyl cellosolve, carbitol, diethylene ether, and diacetone alcohol. The samples produced by the addition of a small amount of these compounds to a resin formed by polymerizing furfurin-furfural with aqueous hydrochloric acid cracked after exposure to the air for a few days.

4. A stearic-acid-aniline-furfural plasticizer.

Reference to the literature in an effort to find previous work on the plasticizing of furfural resins resulted in finding a reference to a patent (10) which advocated the use of a compound formed by the reaction of stearic acid, aniline, and furfural, as a plasticizing agent for furfural resins. To test this compound for its plasticizing ability when applied to the furfurin-furfural resin, equal parts of stearic acid and aniline by weight were heated together. A portion of the resulting liquid was treated with an equal volume of furfural, and boiled for a few minutes. When cool, the

resultant mixture was a black greasy mass resembling graphite grease. The addition of 5 grams of this mixture to a resin formed by adding 15 cubic centimeters of concentrated hydrochloric acid to 50 cubic centimeters of furfurin-furfural solution resulted in a test block which cracked in a few days. A similar test, using a larger amount of the stearic acid compound, was made, also with poor results. The plasticizing compound was modified by decreasing the amount of aniline used, in order to give a harder mass. The use of this compound did not improve the properties of the finished furfural resin.

5. The trial of furfural polysulphide.

Previous work in this laboratory had been done on furfural polysulphide (6). It will be remembered that this polymer is a yellowish, odorous, rubbery mass. The compound is resilient to the degree that it can be worked in the fingers like a stiff putty. In the hope that this resilient feature would be transmitted to the furfurin-furfural plastic, furfural polysulphide was tested as a plasticizing agent.

A quantity of the polysulphide was made up, and 5 grams of it added to 50 cubic centimeters of furfurin-furfural solution. The polysulphide was found to dissolve rapidly. The resulting solution was polymerized by the addition of 15 cubic centimeters of concentrated hydrochloric acid. The resulting solid cracked after removal from the mold within

one day. Samples containing larger precentages of poly-sulphide also cracked in a short time. In view of the odorous character of the sulphide, it was anticipated that resins containing the compound would carry this objectionable odor, however no unusual smell was noticeable.

E. The use of non-aqueous solutions of hydrochloric and sulphuric acid.

1. The action of water.

The first specimen of furfurin-furfural plastic prepared exhibited an undesirable characteristic, which, up to the present writing, had not been fully corrected. This property was that of shrinking, cracking and warping. It had been suspected for some time that the cause of this difficulty was water, which, in vaporizing from the solidified plastic, caused shrinking and warping as it does in poorly seasoned wood. By analogy, the proper procedure in this case would be to adopt proper seasoning, or curing conditions.

a. The use of paraffin. An attempt to find such conditions was made by coating the samples with paraffin. The result of this protection was to delay deterioration, but it did not prevent cracking eventually except in a few cases. Specimens coated with paraffin and allowed to age for two years have been observed to crack after removing the paraffin coating.

b. Dehydrating agents. A second method of removing the water is by means of dehydrating agents. This method was tested by adding various quantities of anhydrous calcium chloride. The salt had little effect other than producing a slight increase in the tensile strength of the plastic. No beneficial results were obtained by keeping the plastic

in a dry condition in a desiccator.

c. The use of anhydrous materials. Another method, and perhaps a more obvious one, is to prevent the liberation of water by using anhydrous materials throughout, and thus prevent the introduction of any moisture. In the preparation of the furfurin solution, the furfural is kept at a temperature which insures the removal of the water as fast as it is formed. This solution, consequently, is practically anhydrous. The acid used contains water, in fact, commercial hydrochloric acid is an aqueous solution. Concentrated sulphuric acid is practically 100% H_2SO_4, so theoretically the use of this acid was acceptable. In attempting to use this acid in its concentrated form, it was found that it produced localized setting of the material, and a plastic was produced that contained numerous small, hard and porous lumps. This non-homogeneous condition was undesirable. The formation of lumps could be avoided by diluting the acid, but of course this defeated the purpose of using sulphuric acid since it added water.

2. The trial of hydrochloric acid gas.

The most obvious solution of the problem was to use non-aqueous solutions of hydrochloric acid. The direct addition of hydrochloric acid gas to the furfurin solution had been attempted, but resulted in the formation of a solid material that was too weak to be of value. Another attempt

to use the gas directly was made by chilling furfural by means of a salt and ice mixture, and passing hydrochloric acid gas into the liquid. It was hoped that a solution of hydrochloric acid in furfural would result, and that due to keeping the solution cold, it would be possible to keep the acid solution for some little time without having it become solid. The furfurin solution and the acid solution could then be mixed in the right proportions, and a plastic containing furfural-furfurin and acid in the right ratio would result. This procedure failed due to the solidification of the furfural after it had absorbed a quantity of the acid gas. As a result of these experiments, it was decided that some neutral solvent would be required to introduce the hydrochloric acid gas into the plastic.

3. The use of alcoholic hydrochloric acid.

The first solvent selected for the trial of non-aqueous solutions of hydrochloric acid was butyl alcohol. This solvent is capable of absorbing large quantities of hydrochloric acid gas, is a good solvent for many organic compounds which can be used as plasticizers, and is relatively inexpensive.

a. The production of saturated alcoholic solutions of hydrochloric acid. For the first few trials, anhydrous hydrochloric acid gas was produced by dehydrating aqueous hydrochloric acid by means of sulphuric acid. The sulphuric acid was simply slowly added to the hydrochloric by means of

a dropping funnel, and the evolved gas was dried by passing it through a tube filled with calcium chloride. However, when it became evident that quantities of dry hydrochloric acid gas beyond the capacity of this simple apparatus were required, a more usable and compact apparatus was assembled for the production of the gas by the action of sulphuric acid on salt. The reaction vessel was a one liter balloon flask, fitted with a reflux condenser and a dropping funnel. The gas coming from the condenser was dried by bubbling through concentrated sulphuric acid, and as a second drying procedure, was passed over anhydrous calcium chloride. In operation, the salt (NaCl) was placed in the flask, and sufficient water added to permit boiling. Concentrated sulphuric acid was then added through the dropping funnel. By controlling the rate of addition of the acid and the amount of heat applied to the flask, a steady evolution of hydrochloric acid gas could be obtained.

The solubility of hydrochloric acid gas in butyl alcohol is such that complete absorption can be obtained by bubbling the gas into the liquid. As the heat of solution is quite high, the alcohol should be kept in a cooling bath. The low temperature also permits a more saturated solution to be formed.

b. Testing the alcoholic solution. After the alcoholic solution was prepared, it was desirable that the

acid content be determined, so that the optimum amounts of solution to be added to the furfurin solution could be estimated. The acid content should also be determined, so that uniform quantities of alcoholic hydrochloric acid could be obtained. A small quantity of the solution was titrated with .1N NaOH in order to determine its normality. The method used for titration was as follows: One cubic centimeters of the solution was removed with a pipette, and added to one hundred cubic centimeters of distilled water. Ten cubic centimeters of the resulting dilute solution were tirated with approximately .1N NaOH. While of course this method did not show the actual amount of hydrochloric acid present, it afforded a convenient method of comparing the various solutions. Difficulty was experienced in removing one cubic centimeter of the concentrated solution with a pipette. The solution at room temperature has a very high vapor pressure, and when it is sucked into a pipette the solution is liable to flash into vapor. For this reason, a suction pump had to be used to fill the pipette. By filling the pipette very slowly, the flashing difficulty was avoided. Bubbles were formed around the pipette when it was placed in the liquid, or when the beaker was touched with the pipette, which also shows the high vapor pressure of the hydrochloric acid solution. It was found necessary to prepare the solution as used, since on standing, the solution became sirupy and turned a dark reddish brown color.

By weighing the alcohol before and after saturation with hydrochloric acid gas, the amount of gas absorbed could be found. The solution was found to contain about 35% HCl. Titration of the alcoholic solution showed it to have a normality about three quarters that of concentrated aqueous hydrochloric acid.

4. The effects of the alcoholic hydrochloric acid.

To test the acid butyl alcohol, it was added in various amounts to fifty cubic centimeters of furfurin-furfural solution. Five trials were made, using five cubic centimeters of the alcoholic acid in the first sample, and increasing the amount of acid each time by five cubic centimeters, so that the last sample contained twenty five cubic centimeters. The first sample failed to solidify within twenty four hours, the second and third samples solidified within a few hours, and the last two samples set so rapidly that overheating occured. The second and third samples, or those containing twenty and thirty percent alcoholic hydrochloric acid, respectively, were found to shrink sufficiently to permit removal from the beaker that was used as a mold within twenty four hours. The samples were hard, glossy, and had a pleasant odor, due to the alcohol content. The samples were found to be less susceptible to cracking than those produced by the use of aqueous hydrochloric acid, but some cracking was still observed. It was evident that a butyl alcohol solution

of hydrochloric acid did not have the property of preventing cracking. The value of the alcoholic acid was its miscibility with plasticizing agents. Dibutyl phthalate was successfully incorporated into the plastic by the use of the alcoholic acid. The use of dibutyl phthalate has been previously discussed.

5. The use of an ethyl alcohol solution of hydrochloric acid.

The various tests were repeated, using an acid prepared by saturating ethyl alcohol with anhydrous hydrochloric acid gas, with results similar to those obtained by the use of the acid butyl alcohol. The tendency of the samples to crack was diminished, but not eliminated.

6. The use of acetone.

Following the trials of alcohols as a solvent, acetone was selected as the next material to act as the carrying agent for the anhydrous hydrochloric acid gas. Results were obtained that called for an extended study of the use of acetone in the production of this type of furfural resin.

a. Reactions. A theoretical consideration of the problem indicates that possibly some effects peculiar to the use of acetone can be anticipated. Acetone can act not only as a solvent for hydrochloric acid gas, but also as a compound capable of forming condensation products with furfural. A pale yellow resin can be prepared by refluxing acetone with furfural, in the presence of a strong caustic solution (35).

In the reaction between furfural and acetone, it has been suggested by Claisen and Ponders that the oxygen of the aldehyde group of furfural splits out two hydrogens of one of the methyl groups of acetone, with the formation of water (12). The condensation product then contains an unsaturated linkage, thus: $-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{|}{C}}-$ to which grouping Herzog and Kreidl attribute the resinifying properties of compounds containing this linkage (21). There is also the possibility that furfural might be added to each methyl group of the acetone molecule, resulting in two such linkages. When these molecules unite, they do so through the oxygen of the original ketone group. On the basis of this theory, two types of compounds would be formed, those having one mol of furfural combined with one mol of acetone, and those containing two mols of furfural per mol of acetone. There would also be various mixtures of these two types.

The plastic formed using acetone is, therefore, the result of two reactions; first, the polymerization of the furfurin-furfural solution by means of acid, and second, the condensation product between furfural and acetone. This condensation product probably polymerizes in the presence of the acid. If a resin similar to that produced by refluxing furfural and acetone in the presence of strong caustic is sought by refluxing the two compounds with acid, an uncontrollable reaction takes place with the formation of a

useless, porous char. This experiment indicates that the condensation product of furfural and acetone is susceptible to polymerization, particularly by acids.

In view of the theory that two reactions take place in the formation of this plastic, it should be possible to vary the properties of the plastic by varying the extent to which each reaction occurs. Control of the reactions can be obtained by varying the amount of acetone added, which will affect the amount of furfural-acetone condensation product present in the final resin.

b. The use of acetone solutions of hydrochloric acid. The first test of acetone was made by following the procedure used in the experiments with alcohols. Acetone was saturated with anhydrous hydrochloric acid gas, and was found to form a solution containing about 35% HCl by weight, at room temperature. Samples were made up by adding the acid acetone to 50 cubic centimeters of furfurin-furfural solution. The amount of acid used was varied from 5 to 30 cubic centimeters in 5 cubic centimeter intervals. Of these samples the specimen containing 15 cubic centimeters of the acidified acetone turned out the best. Larger samples of the plastic containing this ratio of furfurin-furfural solution to acid acetone were made up. They were found much more resistant to cracking than any furfural plastic that had been previously produced. Some of the large pieces cracked slightly, however. It was found that this cracking could be prevented by aging

the plastic in a container in which the atmosphere was kept saturated with acetone vapor. The effectiveness of this method of preventing cracking may be due to the fact that under normal atmospheric conditions acetone vaporized from the plastic before complete reaction took place, and that by saturating the air around the sample, this rate of vaporization could be diminished to such an extent that a nearly complete reaction was produced.

c. The use of sulphuric acid-acetone mixtures. Experiments were next conducted to determine the effect of varying the acetone content, but still keeping the acid content constant. Samples were prepared from furfurin-furfural solution and acid produced by diluting acetone saturated with hydrochloric acid gas with acetone. The samples were too soft and weak to be of value. It was impossible to increase the concentration of acid in acetone, since a saturated solution was being used. A more highly concentrated acid solution could be produced, however, by mixing acetone with sulphuric acid. The use of sulphuric acid is more convenient than the hydrochloric, since the liquid sulphuric acid can be easily mixed with the acetone, while the absorption of hydrochloric acid gas is a much slower process. Sulphuric acid was tested by mixing equal volumes of acetone and acid, and adding 10 cubic centimeters of the resultant solution to 50 cubic centimeters of furfurin-furfural solution. The liquid solidified rapidly, and formed a hard glossy mass,

however it was evident that the material was quite strongly acidic. Other samples were produced using less of the acid mixture, but these samples were inferior to the first sample produced. An acid mixture was formed by mixing 9 parts of acid to 10 of acetone, and various amounts of this solution tried. It was found after trying various amounts of acid solutions resulting from mixing various quantities of acetone and sulphuric acid together that the best samples, as judged by rapid solidification, low acidity, and freedom from cracking, were the result of mixing 10 parts of furfural solution and 2 parts of an acid solution produced by adding 8 parts of concentrated sulphuric acid to 10 parts of acetone.

As a result of these experiments, a series of tests to more accurately compare the various samples was deemed necessary. Samples were prepared in the form of tensile strength briquets, so that the tensile strength of the samples could be used as a basis of comparison. In these samples, the ratio of acetone to sulphuric acid was varied, as was the amount of the acid mixture added to the furfurin-furfural solution. These data are presented in table No. 5.

Table No. 5

The Addition of H_2SO_4-acetone mixtures to the Furfural-furfurin Plastic.

Run No.	H_2SO_4-acetone mixture			Furfurin solution	Age	Strength	Remarks
	H_2SO_4	Acetone	Amt. mix. used.				
	Pts. by vol.	Pts.	Parts	Parts	Days	lbs/sqin	
1 a	50	100	15	100	2	Failed to Set.	
2 a	50	100	20	100	2	0	Still soft.
b					4	50	Slightly soft.
c					6	100	
d					9	200	
3 a	50	100	25	100	2	75	
b					4	125	
c					6	115	Defective.
d					8	150	
4 a	50	100	30	100	2	100	
b					4	225	
c					6	150	Defective.
5 a	50	100	35	100	2	0	Samples cracked.
6 a	60	100	15	100	1	0	Very soft.
b					2	0	Slightly soft.
c					4	50	
d					7	100	

Table No. 5; continued.

Run No.	H_2SO_4-acetone mixture.			Furfurin Solution	Age	Strength	Remarks
	H_2SO_4	Acetone	Amt. Mix. used				
	Pts.(vol)	Parts	Parts	Parts	Days	Lbs/sqin.	
7 a	60	100	20	100	1	0	Still soft
b					2	50	
c					4	100	
d					7	200	
e					12	450	
8 a	60	100	25	100	2	100	Some cracking.
b					4	50	Defective
c					12	250	
9 a	60	100	30	100	2	All samples cracked.	
10 a	60	100	35	100	0	Overheated when mixed.	
11 a	70	100	15	100	3	0	Soft.
b					6	100	
c					11	150	
d					15	250	
e					20	-	Defective.
12 a	70	100	20	100	3	150	
b					6	400	
c					11	650	
d					15	850	
e					20	350	Defective

Table No. 5; continued.

Run No	H_2SO_4-acetone mixture			Furfurin Solution	Age	Strength	Remarks
	H_2SO_4	Acetone	Amt. mix. used				
	Pts.(vol.)	Parts	Parts	Parts	Days	Lbs/sqin	
13 a	70	100	25	100	3	200	
b					6	200	
c					11	200	
d					15	750	
e					20	1050	Failed to break
14 a	70	100	30	100	2	150	Defective. Samples cracked.
15 a	80	100	15	100	1	0	Very soft.
b					2	0	Soft.
c					5	50	
d					10	200	
e					14	175	
f					19	325	
16 a	80	100	20	100	4	450	
b					9	950	
c					13	250	Defective.
17 a	80	100	25	100	5	650	Other samples cracked.
18 a	80	100	30	100	0		Overheated while mixing.
19 a	90	100	15	100	3	150	
b					8	450	
c					10	500	
d					17	600	

Table No. 5; continued.

Run No.	H_2SO_4-acetone mixture			Furfurin Solution	Age	Strength	Remarks
	H_2SO_4	Acetone	Amt. mix. used				
	Pts.(vol)	Parts	Parts	Parts	Days	lbs./sqin	
20 a	90	100	20	100	3	450	No cracking.
b					8	950	
c					12	975	
d					17	1025	
21 a	90	100	25	100	3	--	Samples cracked.

1. Discussion. Inspection of table No. 5 shows that the use of large amounts of the acid-acetone mixture increases the tendency of the samples to crack. The use of acid-acetone mixture in excess of 25 parts of mixture to 100 of furfurin solution produces overheating, with the exception of those cases in which an acid-acetone mixture containing approximately equal volumes of acid and acetone were used. This overheating was anticipated to some extent, due to the large amount of acid used in these cases.

The best samples were produced when 20 parts of acid-acetone mixture were mixed with 100 parts of furfurin solution. The best acid-acetone mixture was found to contain 80 parts of acid to 100 of acetone.

d. The effect of refluxing acetone and furfurin solution.

When sulphuric acid is added to acetone, it will be noted that the mixing is attended by the evolution of heat, and the formation of a red liquid, which rapidly darkens to a deep maroon. The appearance of this color indicates some reaction, probably a polymerization of the acetone by the sulphuric acid. It was thought possible that the ability of the acetone to react with furfural would be diminished by having the acetone already mixed with the acid, and hence being in a polymerized condition. In order to test this theory, 500 cubic centimeters of furfurin-furfural solution were refluxed with 50 cubic centimeters of acetone, and 10

cubic centimeters of sulphuric acid added slowly to 100 cubic centimeters of the refluxed liquid. The result was a resin which was an improvement over previous resins produced by the use of acetone. Blocks of the resin did not crack when exposed to the air over long periods of time. Flat disks made of the plastic warped very slightly. Some of the plastic was cast into the form of balls, which were found to be very resilient, and when allowed to fall on a cement floor, returned four fifths of the distance they had been dropped. An indication that the resin differed chemically was also observed. When a small quantity of resin formed with acid mixed with acetone is diluted with water, a deep purple color will be observed, which persists even in very dilute solutions. If a resin prepared with furfurin-furfural solution refluxed with acetone is diluted, the solution is a dirty brown. The different appearance of these two diluted solutions would seem to indicate a difference in the original resin.

In the resins prepared by mixing acid and acetone, the best results were obtained by the use of 20 cubic centimeters of mixture per 100 cubic centimeters of furfurin solution. Since about half of the acid mixture was acetone, the final resin contained about 10 cubic centimeters of acetone per 100 cubic centimeters of furfurin solution. In the first tests in which acetone was refluxed with furfurin solution, the same amount of acetone was used, that is, 10 cubic centimeters

per 100 cubic centimeters of furfurin solution. It was thought, however, that a larger amount of acetone might prove of benefit when used in the reflux method, hence a series of tests was made in which the furfural solution was refluxed with various amounts of acetone. The samples prepared from the resulting resins were cast in the form of test briquets used in the determination of tensile strength.

1. Presentation of data. The data obtained are presented in table No. 6.

Table No. 6

THE USE OF REFLUXED ACETONE-FURFURIN SOLUTIONS
IN THE PRODUCTION OF FURFURAL PLASTICS.

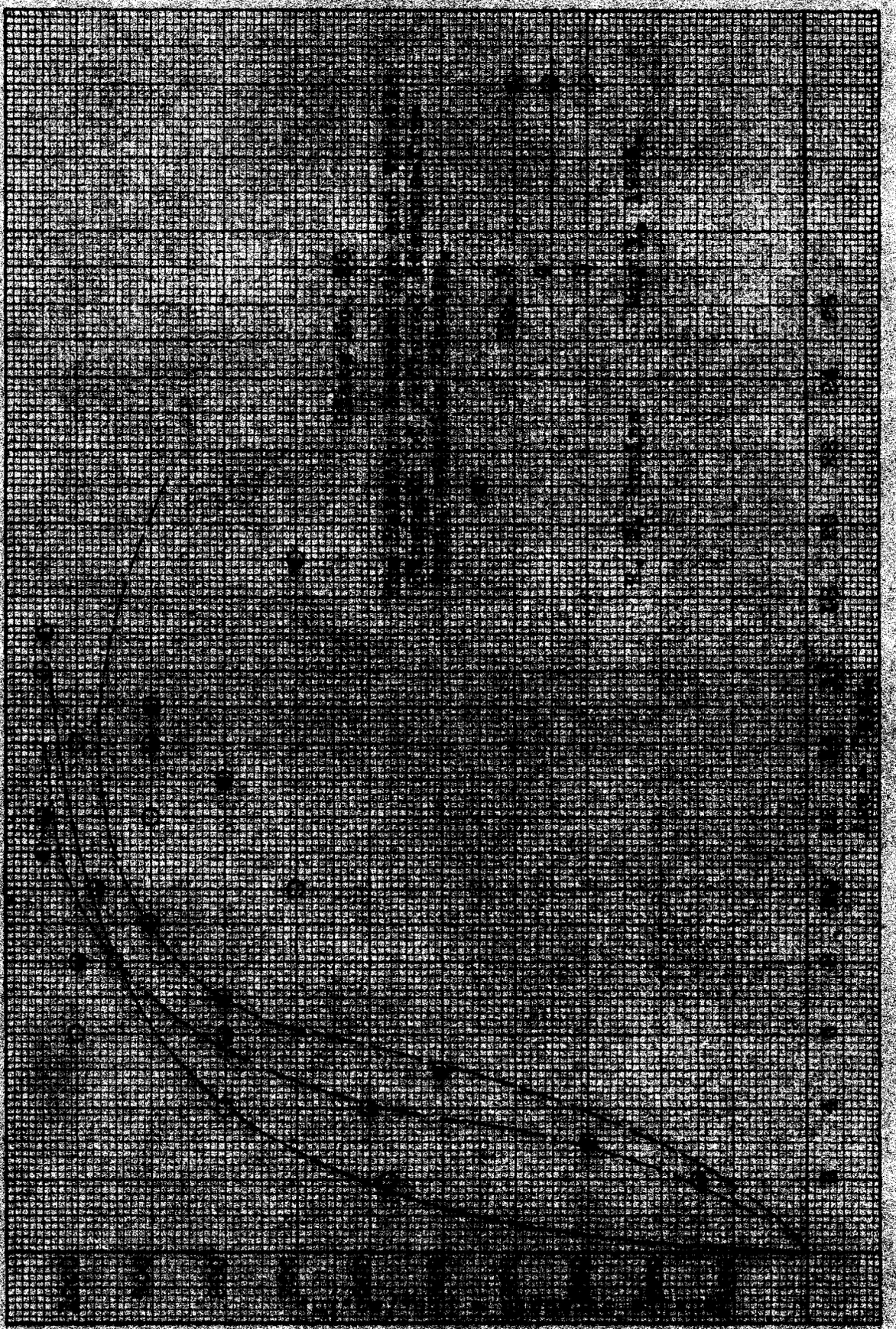
Run No.	Reflux mixture			H_2SO_4	Age	Strength	Remarks
	Furf.Soln.	Acetone	Amt.used				
	Pts. (vol)	Parts	Cu. Cm.	Cu. Cm.	Days	lbs/sqin.	
1 a	10	1	100	10	1	Four samples cracked.	
					2	150	Other samples
					4	200	defective.
2 a	5	1	100	10	3	300	No cracking in
b					5	500	any samples
c					7	800	observed.
d					9	900	
e					11	+1000	Failed to break.
f					13	800	
g					15	900	
h					17	+1000	Failed to break.
i					19	700	
j					21	450	Defective.
3 a	10	3	100	10	2	Remained two days in mold. Samples cracked when removed.	
4 a	5	2	100	10	2	150	Five samples
b					4	600	removed from
c					6	800	mold as soon as
d					8	250 (Def.)	possible; no cracking.

Table No. 6; continued.

Run No.	Reflux mixture			H_2SO_4	Age	Strength	Remarks
	Furf.Soln.	Acetone	Amt.used				
	Pts. (vol)	Parts	Cu. Cm.	Cu. Cm.	Days	lbs/sqin	
4 e	5	2	100	10	8	1000	Five samples in
f					10	975	mold 24 hours;
g					12	+1000	three cracked.
h					14	850	
5 a	2	1	100	10	2	575	Removed from
b					4	800	mold one hour
c					6	1000	after pouring.
d					8	950	No cracking
e					10	700	observed.
f					12	900	
g					14	1000	
h					16	+1000	Failed to break.
6 a	10	1	100	10	2	300	Duplicate Run 1
b					4	500	except removed
c					6	775	from mold as
d					8	780	soon as possible
e					10	800	No cracking
f					12	800	observed.
g					14	700	
h					16	300	Defective.
7 a	10	3	100	10	1	400	Duplicate Run 3
b					3	750	except removed
c					5	1000	from mold as
d					7	975	soon as possible
e					9	+1000	No cracking
f					11	+1000	observed.

Table No. 6; continued.

Run No.	Reflux mixture			H_2SO_4	Age	Strength	Remarks
	Furf.Soln.	Acetone	Amt. used				
	Pts. (vol)	Parts	Cu. Cm.	Cu. Cm.	Days	lbs/sqin.	
7 g	10	3	100	10	13	925	
h					15	+1000	Failed to break.
8 a	5	3	100	10	0	Overheated.	Cracked.
b	5	3	100	8	3	250	
c					5	650	
d					7	775	
e					11	725	
f					13	750	
g					15	900	
9 a	Samples using higher ratios of acetone to furfurin solution overheated when mixed with acid.						



Form E-5

2. Discussion. A study of table No. 6 shows that resins having good tensile strength are produced when a refluxed mixture of acetone and furfurin solution is polymerized with sulphuric acid. When these experiments were carried out, it was found that allowing the samples to remain in the mold after they had solidified increased the tendency of the samples to crack. If the articles were removed from the mold as soon as they were solid enough to handle, no cracking of the material was observed.

There does not appear to be any definite ratio of acetone to furfurin solution at which superior resins are produced. It was found that resins containing more than one part of acetone to two parts of furfurin solution were difficult to handle during molding. The resin containing one part of acetone to ten of furfurin solution has given very good results. It will be noted on plate No. 21 that curve No. 7 rises to a value of over 1000 pounds per square inch at an age of about a week. This curve concerns a resin containing three parts of acetone to ten of furfurin solution.

e. The use of dibutyl phthalate as a plasticizer for acetone-furfural-furfurin resins. Since dibutyl phthalate had been used with some success in previous work, it was tested as a plasticizer in the resin produced by refluxing acetone with furfurin solution, and polymerizing this solution with sulphuric acid. Five cubic centimeters of the phthalate were added to a batch of plastic prepared from 50 cubic centimeters of furfurin solution refluxed with acetone. The resultant plastic had a slightly greasy feeling. With the thought in mind that possibly the phthalate had separated out to some extent, 10 cubic centimeters of acetone were added to five of the phthalate, and this solution added to the resin mixture. A satisfactory product resulted, however the addition of dibutyl phthalate did not improve the product sufficiently to make the use of the plasticizer desirable.

F. The fabrication of tanks.

1. Molds used.

Previous experiments in the production of molded articles have presented a problem in the construction of a proper mold. The adaptation of the furfural plastic to the production of molded tanks proved to be no exception to precedent.

The first mold tried was a small wooden box, the outer surfaces of which were heavily coated with paraffin. The plastic was then shaped around this mold in the form of a box, with sides about half an inch thick. The procedure necessitated the use of a plastic of rather heavy consistency, so that it would not fall off the mold as it was troweled on. The plastic was obtained by the addition of asbestos fiber to the liquid mixture until the desired consistency was reached. The tanks resulting from the use of this mold and molding procedure were unsatisfactory for two reasons. First, it was difficult to remove the wooden form around which the plastic was molded. It was anticipated that the heavy coating of paraffin would permit the removal of the wooden box, however the molded tank adhered so tightly to the box that it had to be broken and removed in sections. Second, the use of a highly filled plastic and the troweling method of application resulted in the inclusion of air pockets in the plastic, which in the finished tank showed up as weak spots and in several cases, a hole completely through the wall of the tank.

The next mold constructed was designed to mold a tank

having inside dimensions of 7½ x 4½ x 4½ inches, with a wall thickness of half an inch. It was a two piece mold, having an inner and outer form. The inner form fitted into the outer so as to leave an annular space, into which the plastic was tamped to form the tank. The surfaces with which the plastic came in contact were coated with paraffin. The outer mold was fastened together at the edges by means of screws, inserted from the outside. In the case of the inner mold, however, provision had to be made so that it could be taken apart from the inside. The inner mold, consequently, was fastened together of means of cleats inside the mold, which were unscrewed when it was desired to remove the inner mold.

This two-piece mold was used with fair satisfaction. The main difficulty encountered was the removal of the bottom piece of the inner mold. This piece was cut to the same dimensions as the inside dimensions of the tank. This construction permitted no convenient method of removing this bottom section. This bottom piece was reconstructed, and made in two pieces with cleats fastened to them in order to have something to grasp when removal was desired. This construction was not satisfactory. The mold was once more rebuilt, this time with a bottom half an inch smaller on each side than the inner dimensions of the tank. The sides of the inner mold were extended half an inch to take care of the space left by diminishing the size of the bottom piece.

When it was desired to remove this mold, the side sections were removed first, after which the bottom section could be removed very easily, in fact it usually came out with one of the side sections. Removal of the inner form was further facilitated by removing it while the plastic was still slightly soft and warm, when the paraffin on the sides of the mold was soft. This soft paraffin served as a lubricant in the withdrawal of the mold.

A similar mold, designed to produce a tank having inside dimensions of 18 x 6 x 6 inches, with a wall thickness of three quarters of an inch, was constructed. The mold was made of heavier material, but the construction features were identical.

2. Mixtures used.

In the first experiments to produce a tank, the molding procedure called for a heavy bodied plastic. This material was formed by the addition of approximately 35 grams of shred asbestos per 100 cubic centimeters of liquid mixture. The tanks produced by this method showed defects resulting from the use of the heavy plastic; it was evident that a more fluid material would produce a better tank. As the tanks are now made, about seventeen grams of asbestos per 100 cubic centimeters of liquid mixture is found to produce a plastic having good molding properties. Other fillers have been used, such as cornstalk and corncob flour, and furfural residue. Best results have been obtained, however, with the use of

asbestos. It has been found that less air will be included in the material if the asbestos is finely groud before mixing it with the plastic. While this procedure deprives the finished material of the strength and binding action of the long fibers, the strength of the resin is such that the slight added strength of the fiber is not of great importance. It is probable that the strength gained by having a more homogeneous material more than compensates for the loss in strength due to the asbestos fiber.

3. Molding procedure.

In the preparation of the plastic, the first step has been to treat furfural with anhydrous ammonia until a 20% solution of furfurin in furfural is formed. The solution is kept at a temperature above 100 °C. to eliminate as much water as possible. Ten cubic centimeters of acetone per 100 cubic centimeters of furfurin solution is then added, and the mixture refluxed until the acetone has combined with the furfural. The length of time required for this reaction is about twenty minutes. The solution is then cooled before further use. In this form the solution may be preserved without deterioration. Technical sulphuric acid is used to polymerize the acetone-furfurin-furfural solution. For the production of small articles, 10 cubic centimeters of acid per 100 cubic centimeters of solution has been found optimum. The acid is added slowly with stirring and cooling. When more than 200 cubic centimeters of material is mixed, more rapid cooling is required than that

obtained by setting the vessel in cold water. The material must be cooled rapidly, which process is accomplished by pouring it out into a flat tray set in cold water. The material is cooled below 35 °C. after which the asbestos filler is added, in case fillers are used. The material solidifies in from 10 to 15 minutes after mixing, hence no delay is permissible in molding after the acid has been added. In the production of larger pieces, such as the large tanks produced, the acid added may be cut down to 8 cubic centimeters per 100 cubic centimeters of solution. Unless this is done, overheating may occur, in spite of thorough cooling before the article is cast.

A modification of this procedure was attempted in order to eliminate to some degree the inclusion of air. The filler was covered with furfurin-acetone solution, and allowed to stand until thoroughly saturated. A plastic was then made with an excess of acid, so that when the filler was added, the correct ratio of solution, acid and filler would result. Difficulty was encountered, however, in the formation of a plastic containing an excess of acid. Despite care, and very thorough cooling, the material overheated before the filler could be added. As a result this modification of the procedure could not be used.

In placing the material into the mold, it should be poured in in such a manner as to include the least possible amount of

air. In order to prevent the trapping of air on the under side of the inner mold, the first few portions of the plastic are poured into the mold before the inner form is placed into position. When the inner mold is inserted, it is rocked back and forth, so that all the air beneath it is displaced, after which the inner form is screwed down into position. When the mold is nearly full, it has been found beneficial to stir the material slightly, which action removed air bubbles which stick to the walls of the mold. Every precaution should be observed to obtain a dense, homogeneous structure in the finished tank.

The liquid material polymerizes to a yielding solid material in about ninety minutes, which reaction is accompanied by a rise in temperature. If the plastic has been thoroughly cooled before molding, this temperature rise will not be so great as to cause damage. The increase in temperature is of assistance in the removal of the inner form, since it softens the paraffin coating of the mold, and permits the form to be removed without difficulty. The outer mold should be removed at the same time, and the solid although still soft tank is placed upon slats, so as to permit free circulation of air during the curing period. Unless this is done, the bottom of the tank will warp badly. The tank will be hard, rigid and ready for use within a week after molding. In some cases a slight warping of the sides has been observed, which can be corrected by placing wooden strips across the top of the tank,

and holding the sides in position. These strips should be applied as soon as the tendency of the tank to warp is observed.

4. The testing of tanks.

Several physical tests were made on the tanks in order to determine their suitability for commercial application.

a. The loss in weight by aging. One of the more noticeable characteristics of the articles was their decrease in weight. Data were taken on this loss in weight over some period of time.

1. Presentation of data. These data are presented in table No. 7, and curve No. 22.

Table No. 7

The Effect of Age on the Weight of Tanks

Age (days)	Weight in grams. Tank No. 1-A	2-A	3-A	4-A
0 (initial)	1905	2176	2178	2035
1	1828			
2	1791			
3				1962
4			2049	
5		2035		
6	1709			
7			2009	
8		2002		
9	1693			
14				1820
19		1892		
20	1648			

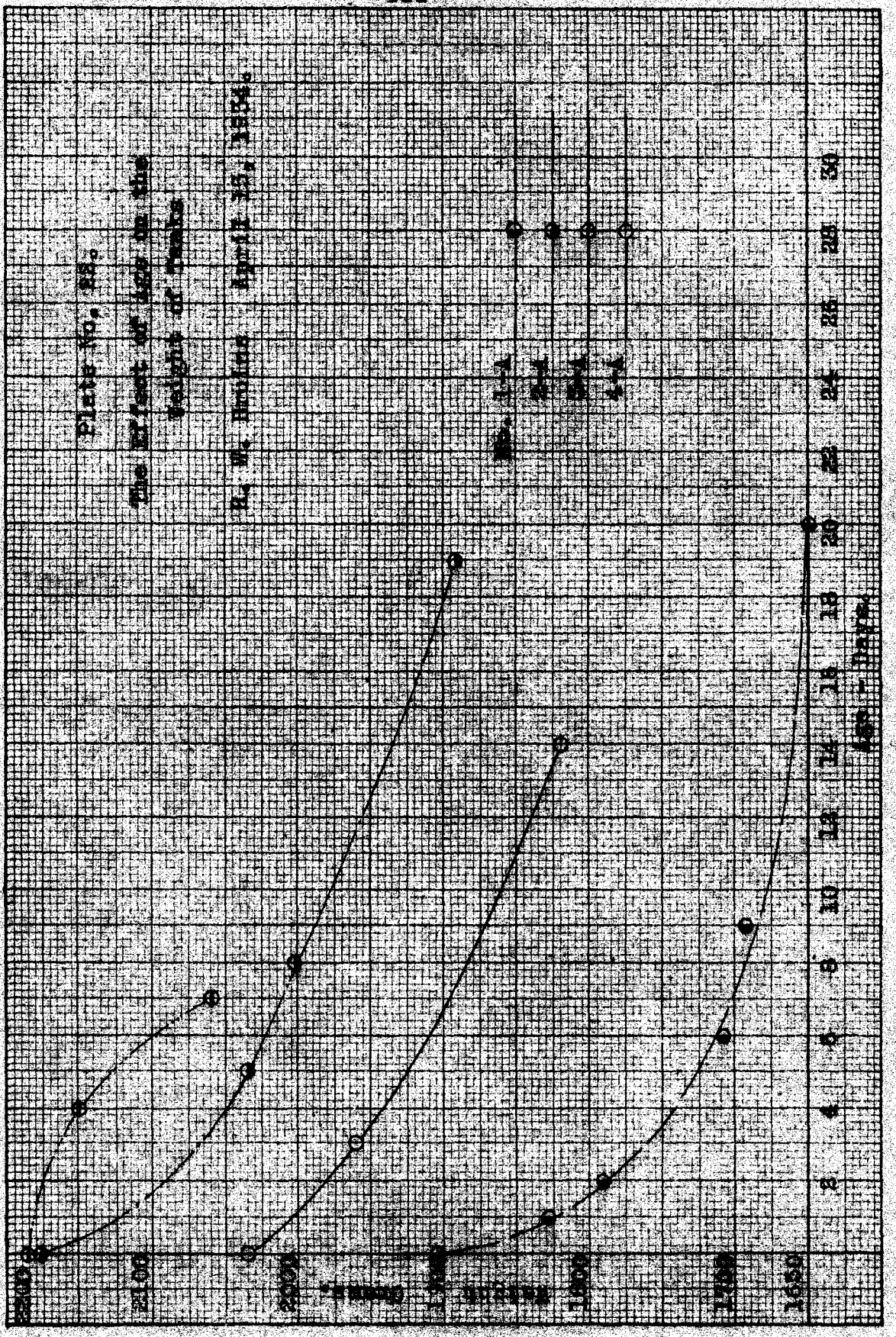


Plate No. 85.
The Effect of Age on the Height of Peak
at W. Hughes April 25th 1956.
Kgs. - Pressure
Time Minutes

2. Discussion. The decrease in weight indicates that some constituents of the plastic do not react, and are slowly liberated. The materials are probably furfural and sulphuric acid.

b. Shrinking. Another of the more noticeable properties of the tanks is their tendency toward shrinking. This shrinking takes place while the article is fairly new, most of the shrinking occuring during the first week. The amount of shrinking is rather large. The inside dimensions of the outer mold for the small tank measures $8\frac{1}{2}$ x $5\frac{1}{2}$ inches at the bottom. A tank cast in this mold, after it was about one month old, measured 8 1/8 x 5 1/4 inches. In the case of the larger tanks, the same dimensions for the mold are 19 3/8 x 7 1/4 inches. The finished tank measured 18 3/16 x 6 7/8 inches. It is surprising that the tanks do not warp or crack in view of this large shrinkage. It is evident that the shrinkage must be uniform, and due to the symmetrical shape of the tank, cracking does not occur.

Due to the shrinkage, the plastic in its present stage of development would be unsuitable for use as an acid proof lining for a tank already constructed. The large amount of shrinking would cause separation of the lining from the tank wall. In cases where the entire tank can be constructed of the plastic, the material may be used with satisfaction, since the mold can be made such a size that the finished tank,

after it has shrunk to its final form, will have the desired dimensions.

c. Resistance to corrosion. Synthetic resins in general are noted for their resistance to chemical corrosion. The furfural plastic under discussion is no exception to the rule, in fact it is more resistant than many of the commercial resins. Bakelite, for example, is not recommended for use with caustic solutions or with organic solvents, particularly acetone. Both of these compounds have been kept in tanks made of the furfural plastic without deterioration of the tank, although a darkening of the liquid was observed, doubtless due to the solution of free furfural in the tank.

Of particular interest is the resistance of the plastic toward corrosion by hydrofluoric acid. Ceramic apparatus and glass lined equipment, while widely recommended for use under very corrosive conditions, do not withstand the action of hydrofluoric acid. Several small dishes were molded of the plastic without the addition of filler, since the asbestos filler, being a silicate, would be attacked by the acid. The dishes were filled with aqueous hydrofluoric acid. After ten days the dishes were washed and examined; they had not been damaged by the acid.

d. Gain in weight due to filling with aqueous solutions. Several tanks were tested over long periods of time in order to determine their resistance to corrosion by a few of the

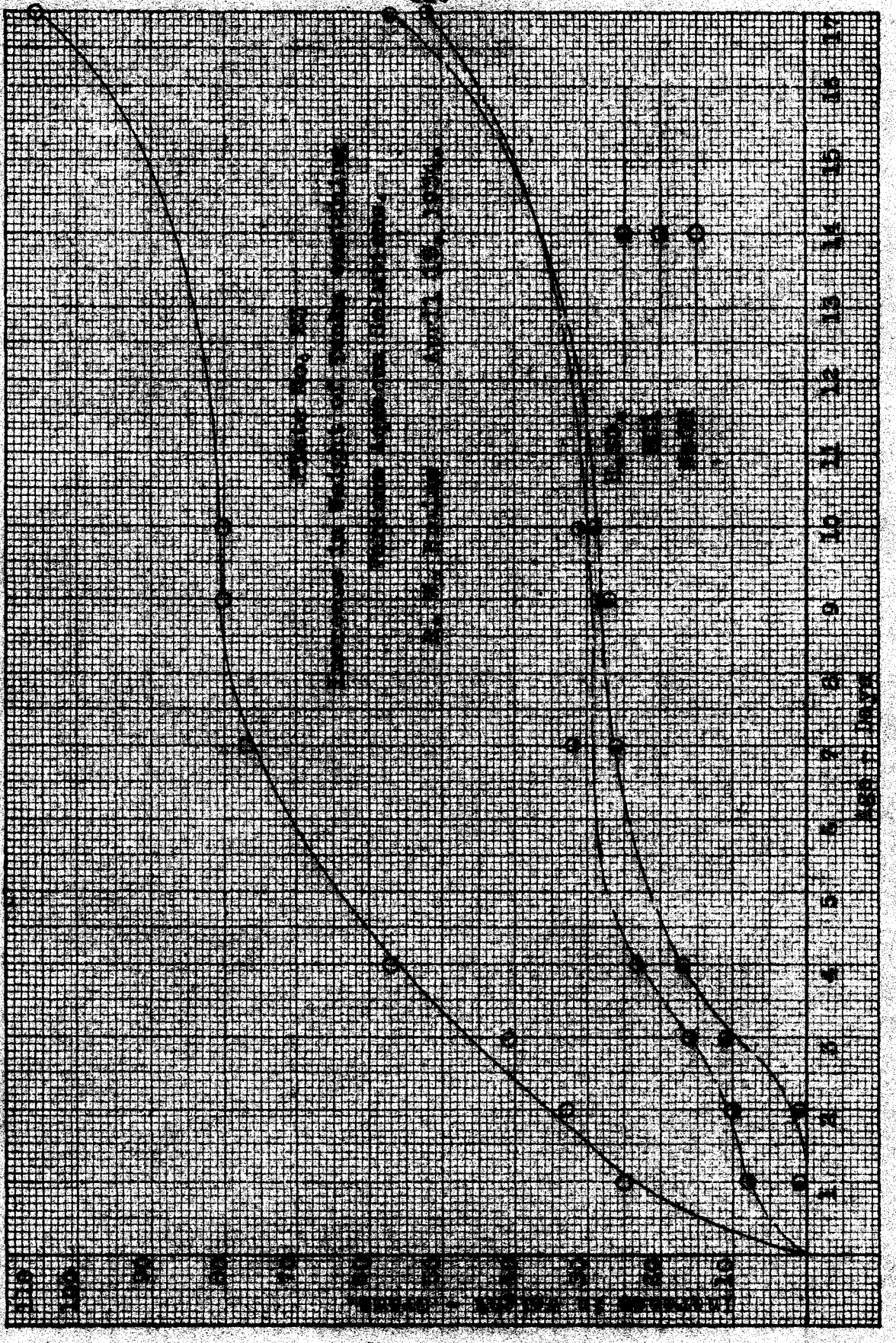
more common industrially used materials. Tanks were filled with 10% solutions of sulphuric acid, hydrochloric acid and caustic soda. The tanks were weighed from time to time, particularly toward the start of the test, so as to obtain data on the change in weight.

1. Presentation of data. These data are presented in table No. 8, and in graphical form on plate No. 23.

Table No. 8

The Effect of Various Aqueous Solutions on the Weight of Tanks.

Age - days.	Weight in grams.					
	H_2SO_4		HCl		NaOH	
	Wt.	Gain	Wt.	Gain	Wt.	Gain
Initial dry weight	1648	0	1892	0	2084	0
1	1649	1	1900	8	2109	25
2	1649	1	1902	10	2117	33
3	1659	11	1908	16	2125	41
4	1665	17	1915	23	2141	57
7	1674	26	1924	? 32	2161	77
9	1675	27	1920	28	2164	80
10	1677	29	1923	31	2164	80
17	1705	57	1944	52	2190	106



2. Discussion. Plate No. 23 presents the gain in weight of tanks filled with 10% solutions of sulphuric acid, hydrochloric acid and caustic, respectively. It will be noted that the gain in weight for the two acids is practically the same, while the gain in weight for the tank filled with 10% caustic solution is somewhat higher. The larger gain in weight for the caustic tank should not be interpreted to necessarily mean that the caustic causes more penetration. There may be differences in the structure of the tank walls sufficient to account for the higher values.

e. The effects of alternate soaking and drying. An important point to bear in mind when liquids are kept in the tank is that the plastic does absorb some moisture. As a result, when the tank is drained, the absorbed moisture is slowly eliminated from the material, and the tank warps badly, in fact to the extent of causing rupture. In the event that a tank is not being used for some time, instead of draining it and leaving it dry, the tank should be refilled with water, so as to prevent drying out. If this precaution is not observed, the tank will warp and probably crack.

5. The estimated cost of materials for a battery box molded from the acetone-furfurin-furfural plastic.

This estimate of the cost of materials of a battery box is based upon a box having outer dimensions of $10\frac{1}{2}$ x 7 inches at the base, and a height of $9\frac{1}{2}$ inches. The wall thickness is one half inch. The box is equipped with two spacers to divide the box into three cells; these spacers measure 6 x 9 inches, and are one quarter of an inch thick. A hand grip is molded at each end of the box.

Outside dimensions: $10\frac{1}{2}$ x $9\frac{1}{2}$ x 7 inches.
Inside dimensions: $9\frac{1}{2}$ x 9 x 6 inches.

Outside volume: 668 cu. in.
Inside volume: 513 cu. in.
Volume of plastic: 155 cu. in.

Volume of spacers: $2(6x9)(\frac{1}{4}) = 27$ cu.in.
Volume of hand grips: 5 cu. in.

Total volume of plastic: 187 cu.in.

This is the final volume. Shrinkage is 7%, based on the final size, hence the original amount of plastic required is $\frac{187}{.93}$ or 203 cu. in. The slight increase in volume when filler is added will be neglected.

The volume of materials required is:

$$203\ (.09) = 18.27 \text{ cu. in. of sulphuric acid.}$$

$$(203 - 18.27)(.1) = 18.5 \text{ cu. in. of acetone.}$$

$$203 - 18.27 - 18.5 = 162. \text{ cu. in. of furfurin solution.}$$

The weight of materials required is:

$$\frac{18.27(62.4)(1.8)}{1728} = 1.188 \text{ lbs. sulphuric acid.}$$

$$\frac{18.5(62.4)(.8)}{1728} = .534 \text{ lbs. acetone.}$$

$$\frac{162(62.4)(1.19)}{1728} = 6.96 \text{ lbs. furfurin solution.}$$

This solution is 2.6% ammonia. Hence .18 lbs. of ammonia, and 6.78 lbs. of furfural are required.

Asbestos filler at $25 per ton is used. Two and a half grams of asbestos per cubic inch of plastic is required. The amount of asbestos required is

$$\frac{203\ (2.5)}{454} = 1.1 \text{ pounds asbestos.}$$

The cost of materials for the battery box is

1.188	lbs.	H_2SO_4	@ 2¢	= $ .0236
.534	lbs.	acetone	@ 12¢	= .064
.2	lbs.	ammonia	@ 16¢	= .032
6.78	lbs.	furfural	@ 10¢	= .678
1.1	lbs.	asbestos	@ 1½¢	= .014

Estimated cost for materials = $ .811

The material cost is high, largely due to the expense for furfural. The design of the box could possibly be altered, using thinner sections. If this could be done, and the price of furfural lowered, a battery box molded from the furfural plastic would be commercially possible.

2. THE TREATMENT OF FURFURAL WITH SULPHUR DIOXIDE.

A. First experiments.

The addition of hydrogen sulphide to furfural had been shown by previous experiments to produce an interesting furfural derivative (6). In the hope that other interesting sulphur-furfural combinations might be obtained, a quantity of furfural was treated with gaseous sulphur dioxide. The gas was bubbled through the furfural, in which it very rapidly dissolved, indicating either high solubility, easy addition to furfural, or possibly both. Judging from the fact that quite a large amount of heat was liberated during the treatment, an addition product of sulphur dioxide and furfural was formed. The furfural darkened rapidly during treatment, and at the end of the procedure had a very strong odor of sulphur dioxide.

B. The effect of hydrochloric acid.

Since the furfurin-furfural plastic is produced by the addition of hydrochloric acid to a solution of furfurin in furfural, it was thought that possibly a plastic might result from the addition of hydrochloric acid to furfural treated with sulphur dioxide. A quantity of furfural was treated with sulphur dioxide for one hour, and concentrated hydrochloric acid added in the ratio of 30 parts of hydrochloric acid to 100 of furfural treated with sulphur dioxide. Unlike the reaction following the addition of acid to furfurin solution, very little heat was evolved, and the liquid solidified to a soft jelly in about an

hour. There was a pronounced odor of sulphur dioxide. After several days, the odor had practically disappeared, and the material formed was a soft, carbon-like material. Since a test tube had been used as a mold, the outer surfaces of the sample were shiny, but the interior was soft, porous, and highly absorbent, as was discovered when the tip of the tongue was applied to test the acidity. This rod of material was found to be soft enough to use as a marking crayon, but due to the smooth, shiny exterior, did not soil the fingers.

1. The determination of density.

In the experiments up to this point, the furfural had been treated with sulphur dioxide for one hour, bubbling the gas through the furfural in a slow stream. The amount of sulphur dioxide introduced into the furfural was determined by weighing the liquid before and after treatment. It was found to contain 8.5% sulphur dioxide, that is, for every 100 grams of liquid, 8.5 grams of sulphur dioxide were present. It was desired to find the effect of increasing the sulphur dioxide content, and to note what properties were imparted by the use of varying amounts of hydrochloric acid. Samples in the form of short cylindrical rods were molded from furfural containing 8 and 16% sulphur dioxide and various amounts of hydrochloric acid. A similar group of samples was prepared from furfural treated with oxygen for two hours, and included for the sake of comparison. After the samples had dried, their density was determined. Density was selected as a

basis for comparison since it was desired to test the comparative hardness of the samples, and density could be easily obtained by weighing, while actual testing of the samples by marking with them would be difficult to compare on a definite basis.

The first series was produced from furfural that had been treated with sulphur dioxide until it contained 8% of the gas. The hydrochloric acid content was varied in 10% steps from 0 to 100% by volume of the amount of the furfural solution used. The piece containing 10% of hydrochloric shrunk and cracked very badly. The piece containing 20% did not crack, but shrunk quite a lot. The specimens containing from 30 to 60% inclusive were the best of the series. They shrunk enough to permit removal from the mold by pushing them out with a rod. They had a hard surface, with a soft inner core, and marked well. The crayon containing 40% hydrochloric acid was, in the writer's opinion, the best, as it was soft enough to mark easily, and still made a very deep black mark. The pieces containing higher percentages of hydrochloric acid, while being soft enough to write easily, had more of a gray color. Also the pieces containing hydrochloric acid in an amount above 60% did not shrink enough to allow the mold to be taken off by any method other than breaking it off. This series required about a week of aging before the specimens lost their odor of sulphur dioxide and hydrochloric acid.

The second series contained furfural that had been treated with sulphur dioxide until it contained 16% of the gas. The hydrochloric acid content was varied as in the previous series. As in the case of the first series, the crayon containing 10% hydrochloric acid shrunk and cracked badly. The best crayons contained from 10 to 50% hydrochloric acid, and that containing 50% was considered the best. Shrinkage was so low in the crayons containing from 60 to 100% hydrochloric acid inclusive that the molds had to be broken off.

The third series was made up using hydrochloric acid in 10% steps from 0 to 100% by volume of the amount of furfural solution used, as in the previous series, but substituting furfural treated with oxygen for 2 hours. The middle members of the series were found to be the best, as the crayons containing small amounts of hydrochloric acid shrunk, and those containing above 60% hydrochloric acid were too gray.

The density of the samples and their composition is presented in table No. 9. A graphical presentation is found in plate No. 24, where density is plotted as the ordinate and hydrochloric acid content the abscissae.

Table No. 9.

The relation of the hydrochloric acid content to the density of furfural plastics.

Series 1. The use of furfural containing 8% sulphur dioxide.

HCl cont. % of furf.	Dimensions (cm) Lgth.	Diam.	Volume Cu.cm.	Weight Gms.	Density Gms./cc.
10	Sample cracked and warped.				
20	6.0	1.2	6.78	3.480	.513
30	9.6	1.25	11.78	6.524	.554
40	11.5	1.3	15.26	8.456	.555
50	10.5	1.25	12.90	7.602	.589
60	11.8	1.3	15.67	8.251	.527
70	10.9	1.3	14.48	7.126	.492
80	4.0	1.3	5.30	2.644	.500
90	7.5	1.35	10.78	4.878	.453
100	8.0	1.3	10.60	4.700	.444

Series 2. The use of furfural containing 16% sulphur dioxide.

HCl cont. % of furf.	Dimensions (cm) Lgth.	Diam.	Volume Cu.cm.	Weight Gms.	Density Gms./cc.
10	Sample cracked and warped.				
20	10.6	0.9	6.38	6.725	1.050
30	11.8	1.0	9.27	9.038	.975
40	12.2	1.25	15.00	10.603	.707
50	11.8	1.3	15.70	10.400	.664
60	12.1	1.3	16.10	10.703	.665
70	7.6	1.4	11.70	7.248	.620

Table No. 9 (cont.)

Series 2. The use of furfural containing 16% sulphur dioxide.

HCl cont. % of furf.	Dimensions (cm) Lgth.	Diam.	Volume Cu.cm.	Weight Gms.	Density Gms./cc.
80	5.0	1.3	6.65	4.658	.70 ?
90	11.0	1.3	14.60	7.730	.540
100	7.5	1.33	10.40	5.802	.560

Series 3. The use of furfural treated with oxygen for 2 hrs.

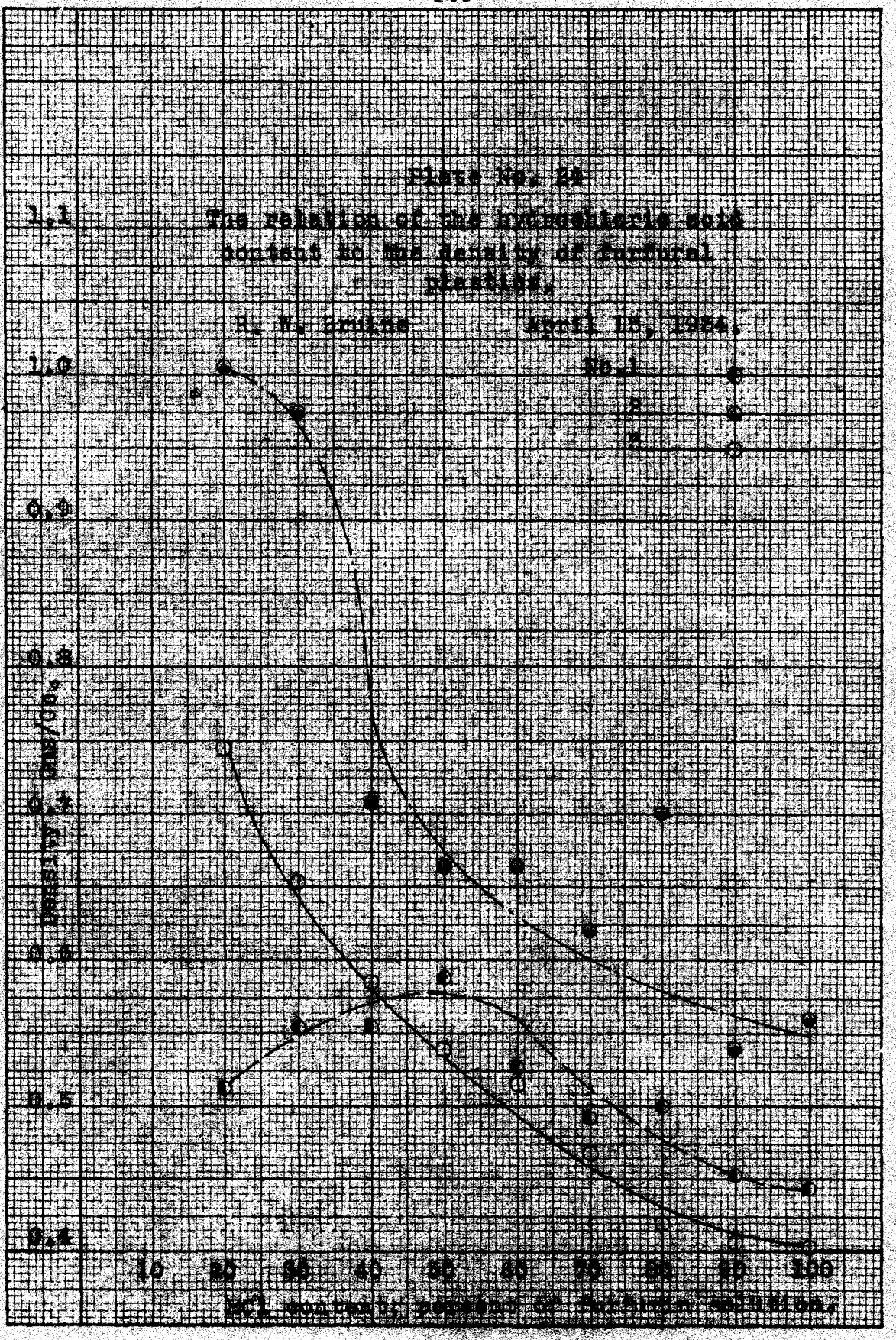
HCl cont. % of furf.	Dimensions (cm) Lgth.	Diam.	Volume Cu.cm.	Weight Gms.	Density Gms./cc.
10	Sample cracked and warped.				
20	8.3	1.0	6.52	4.836	.746
30	9.7	1.1	9.20	6.016	.653
40	9.7	1.2	10.97	6.422	.585
50	11.0	1.25	13.50	7.290	.540
60	12.0	1.3	15.92	8.242	.517
70	11.0	1.35	15.78	7.386	.468
80	8.8	1.35	12.60	5.288	.420
90	6.0	1.35	8.58	3.491	.407
100	6.5	1.30	8.63	3.470	.403

Form E-5

Plate No. 28

The relation of the methacrylic acid contents to the density of furfural plastics.

R. W. Emulns April 25, 1944.



a. Discussion of curves. Two of the curves, that of the oxygen-furfural plastic and that of the material containing 16% sulphur dioxide were about what one would anticipate; the other curve is rather surprising. Due to the elimination of excess hydrochloric acid, one would suppose the density of the samples to drop. However in the case of the material containing 8% sulphur dioxide, the density rose to a maximum at about 50% hydrochloric acid--the mixture used in producing the best writing specimen of the series.

2. Substitute lead pencils.

Since the hardness of the material is readily controlled by using suitable amounts of acid, it was thought that it might be possible to produce "lead" pencils having a graded degree of hardness, such are as used for drawing purposes. The wooden sheath of a lead pencil was plit lengthwise, the lead removed, and the two halves of the sheath glued together. The resulting tube was filled with the liquid mixture. A "lead" of satisfactory writing qualities was produced, however the material was quite brittle. Difficulty was also encountered in sharpening the pencil, as the synthetic lead broke off quite easily.

3. Compressing the material.

In an attempt to produce a crayon of more satisfactory wearing and color properties, some of the material produced with the use of sulphur dioxide was ground and pressed in a suitable mold to form a more compact crayon. Difficulty was encountered in getting the material to stick together.

To overcome this difficulty, the powder was mixed with a small amount of Bentonite (10% by weight of the powdered crayon material). Several good crayons were produced by this method, although it required careful regulation of pressure to get a crayon that would be of a proper degree of hardness to write satisfactorily. It was observed that the pencils produced by compressing the material did not have a uniform hardness. The end of the crayon next to the movable plunger was narder than the other end; also the pencil broke off as if it had been formed from disks, or laminations pressed together. These two defects indicate an uneven application of pressure.

4. The decrease in weight.

It was noted that the material lost weight rapidly as its age increased. Part of this loss in weight was due to the elimination of hydrochloric acid and sulphur dioxide, however the loss was so great that it was thought that possibly some of the material might be subliming. A second possibility to account for the loss was that the reaction was not complete, and that the unchanged furfural was vaporizing. To test this theory, runs were made with solutions of furfural containing 8, 16 and 24% sulphur dioxide. These runs were made simultaneously, and treated identically, starting with 300 grams of material in each case. The products were weighed over some period of time, and the decrease in weight noted. The data are presented in table No. 10.

Table No. 10.

The decrease in weight of the SO_2-treated furfural plastic.

No.	SO_2 content (%)	Age (days)	Weight (Gms.)
1	8	0 (initial)	300
		1	187
		7	118
		11	118
2	16	0 (initial)	300
		1	195
		7	134
		11	127
3	24	0 (initial)	300
		1	198
		7	134
		11	127

It can be seen from the data presented in table No. 10 that the addition of larger amounts of sulphur dioxide does not prevent the loss in weight.

5. The effect of addition to the furfurin solution.

A resin was formed by the addition of equal parts of furfurin solution and an 8% solution of sulphur dioxide in furfural. The resin formed was too hard to be used as a crayon, and had a strong odor of sulphur dioxide. It was not resistant to cracking, as the sample checked within a few hours.

C. The production of furfural crayons.

Preliminary experiments had shown that a furfural resin having a soft carbon-like texture could be produced by polymerizing a solution of sulphur dioxide in furfural by means of hydrochloric acid. Somewhat similar products could be produced if furfural treated with oxygen was used. Several series of tests were made on resins in which mixtures of these two furfural solutions were used. Since it had been shown that the amount of hydrochloric acid used had quite an influence on the hardness of the material, the hydrochloric acid content was varied in order to obtain a series of samples having a varied degree of hardness.

1. The method of procedure.

Eleven series of crayons were molded, in which the furfural used was treated with oxygen and sulphur dioxide. A total of 50 cubic centimeters of furfural solution was used

in each test. In the first series, 50 cubic centimeters of SO_2-treated furfural was used, omitting the oxygen treated furfural. The hydrochloric acid content was varied from 5 to 50 cubic centimeters in intervals of 5 cubic centimeters, so as to obtain a difference in the hydrochloric acid content of 10% between samples, expressed as a percentage of the amount of furfural solution used. In the second series, 45 cubic centimeters of SO_2-treated furfural, and 5 cubic centimeters of oxygen treated furfural were used with the various amounts of hydrochloric acid. In this way eleven series were made, each series having ten samples. In all the series furfural containing 8% sulphur dioxide was used, and in the case of treatment with oxygen, the gas was bubbled through the furfural for two hours.

After the various liquids had been thoroughly mixed, the material was poured into the molds, consisting of glass tubing fitted with a cork at one end. After the material had solidified, the cork was removed, and the crayon pushed out of the mold; it was then allowed to dry. After a week of drying, the material had lost its odor of sulphur dioxide and hydrochloric acid.

In order to test the various crayons, a line was drawn with each. To produce comparative lines, it was essential that the testing conditions be the same in each case. The crayons were ground to a chisel shaped point, care being

taken to produce similar points on the various samples. The pressure of the crayon on the paper was regulated by clamping the crayon in a vertical position at the end of a hinged arm, and by placing weights on this arm, the desired pressure could be obtained. The lines were produced by pulling a strip of paper beneath the crayon, in which operation a pair of paper guides were found helpful in drawing a straight line.

2. Presentation of data.

Because of the similarity of the eleven series, the data presented here will be limited to a typical series, No. 4. This particular group was selected for the reason that it clearly shows the gradation in hardness produced by the use of various amounts of hydrochloric acid. In table No. 11 will be found the compositions of the various samples, and the corresponding marks are presented in plate No. 25.

Table No. 11

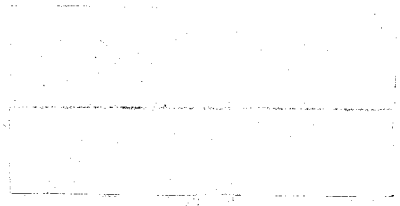
The composition of furfural crayons.

Series No. 4.

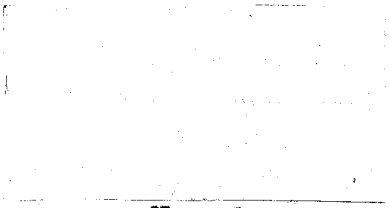
Sample No.	Furfural SO_2 treated Cc.	Furfural O_2 treated Cc.	HCl Cc.	HCl % of furf.	Remarks
1	30	20	5	10	See
2	30	20	10	20	plate
3	30	20	15	30	No.
4	30	20	20	40	25.
5	30	20	25	50	
6	30	20	30	60	
7	30	20	35	70	
8	30	20	40	80	
9	30	20	45	90	
10	30	20	50	100	

Plate No. 25.

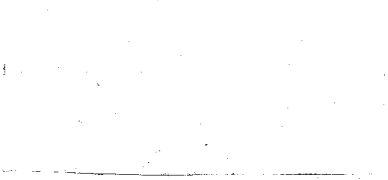
Lines made by samples. Series No. 4.



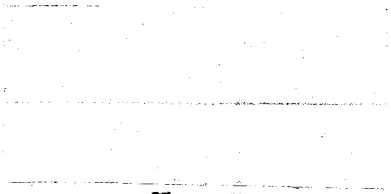
No. 1



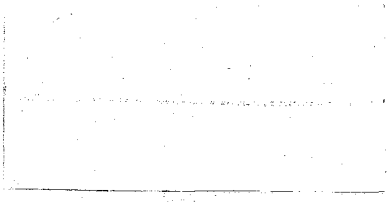
No. 6



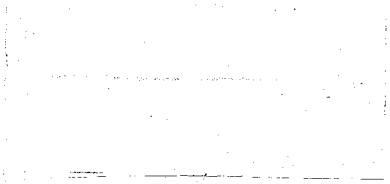
No. 2



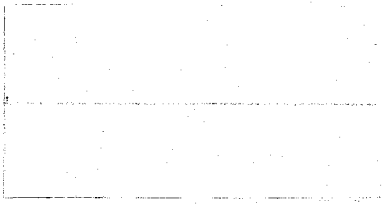
No. 7



No. 3

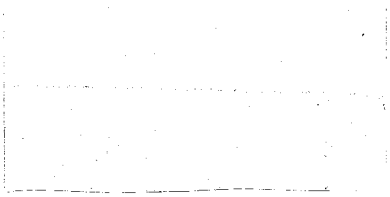


No. 8

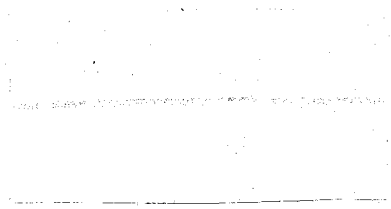


No. 4

No. 9



No. 5



No. 10

3. Discussion of data.

It will be observed from an inspection of the marks produced by the various samples that the hardness of the crayons decreases as the hydrochloric acid content is increased. The samples containing a small amount of acid have a gray cast, but the color deepens as the acid is increased, and finally the gray begins to appear once more, probably due to dilution of the resin by the acid. The pencils containing equal amounts of furfural solution and acid are so soft that they may be crushed between the fingers. In the respect that a graded hardness series may be produced, the furfural crayons are superior to the charcoal sticks that are usually used for sketching purposes. The crayons were further tested by actual use. A complete set of crayons in this series was prepared and presented to the Architectural Engineering Department of Iowa State College, where they were tested by the students and staff. They were pronounced equal in quality to the standard charcoal sticks, from the standpoint of covering power and permanence when treated with a fixative solution in the usual manner.

4. The cost of materials.

Basis: One cubic foot of material. Composition: 6 parts SO_2 treated furfural (8%), 4 parts oxygen treated furfural (2 hours treatment), and 5 parts hydrochloric acid (39%) by volume. The resin produced using this formula weighs

approximately 35 pounds per cubic foot.

Total number of parts: 6 + 4 + 5 = 15.

SO_2 treated furfural required: $\frac{6}{15}(1) = 2/5$ cu.ft.

$\frac{2}{5}(62.4)(1.16) = 29$ pounds furfural.

SO_2 required: $\frac{29(.08)}{.92} = 3.53$ pounds SO_2.

Oxygen treated furfural required: $\frac{4}{15}(1) = \frac{4}{15}$ cu.ft.

$\frac{4}{15}(62.4)(1.16) = 19.3$ pounds furfural.

Oxygen required: 100 cc/liter furfural/min.

$\frac{100\ (120)(19.3)}{2.53\ (28317)} = 3.24$ cubic feet.

Hydrochloric acid required: $\frac{5}{15}(1) = \frac{1}{3}$ cu. ft.

$\frac{1}{3}(62.4)(1.19) = 24.5$ pounds acid.

Furfural:	29	19.3	48.3 lbs.	@ 10¢	= $ 4.83
SO_2			3.53 lbs.	@ 7¢	= .24
O_2			3.24 cu.ft.	@ 2¢	= .07
HCl			24.5 lbs.	@ 2¢	= .49

Material cost per cubic foot = $ 5.60

Cost per cubic inch $\frac{5.60}{1728} = \$0.00324$.

Estimated cost for a crayon 3 inches long, 3/8 inches in diameter. Volume of crayon: $\frac{(3/8)^2(\pi)(3)}{4} = .331$ cu.in.

Material cost for crayon: .331 (0.00324) = $0.001.

Since one cubic foot of material weighs 35 pounds, the cost per pound is: $\frac{5.60}{35} = \$0.16$.

3. THE DESIGN OF A PLANT FOR THE PRODUCTION OF FURFURAL-BASE MOLDING COMPOUNDS.

Since the furfural resins have been developed to the point of possible commercial application, the design of a plant for the production of the molding liquid is of interest. The plant described in the following pages is designed to produce sufficient molding material for the fabrication of one thousand battery cases per day. The amounts of the various materials required for a typical case has already been calculated (see page No. 118). The daily raw material requirements will be 7500 pounds, or 776 gallons of furfural, 77.6 gallons of acetone, and 85.3 gallons of sulphuric acid.

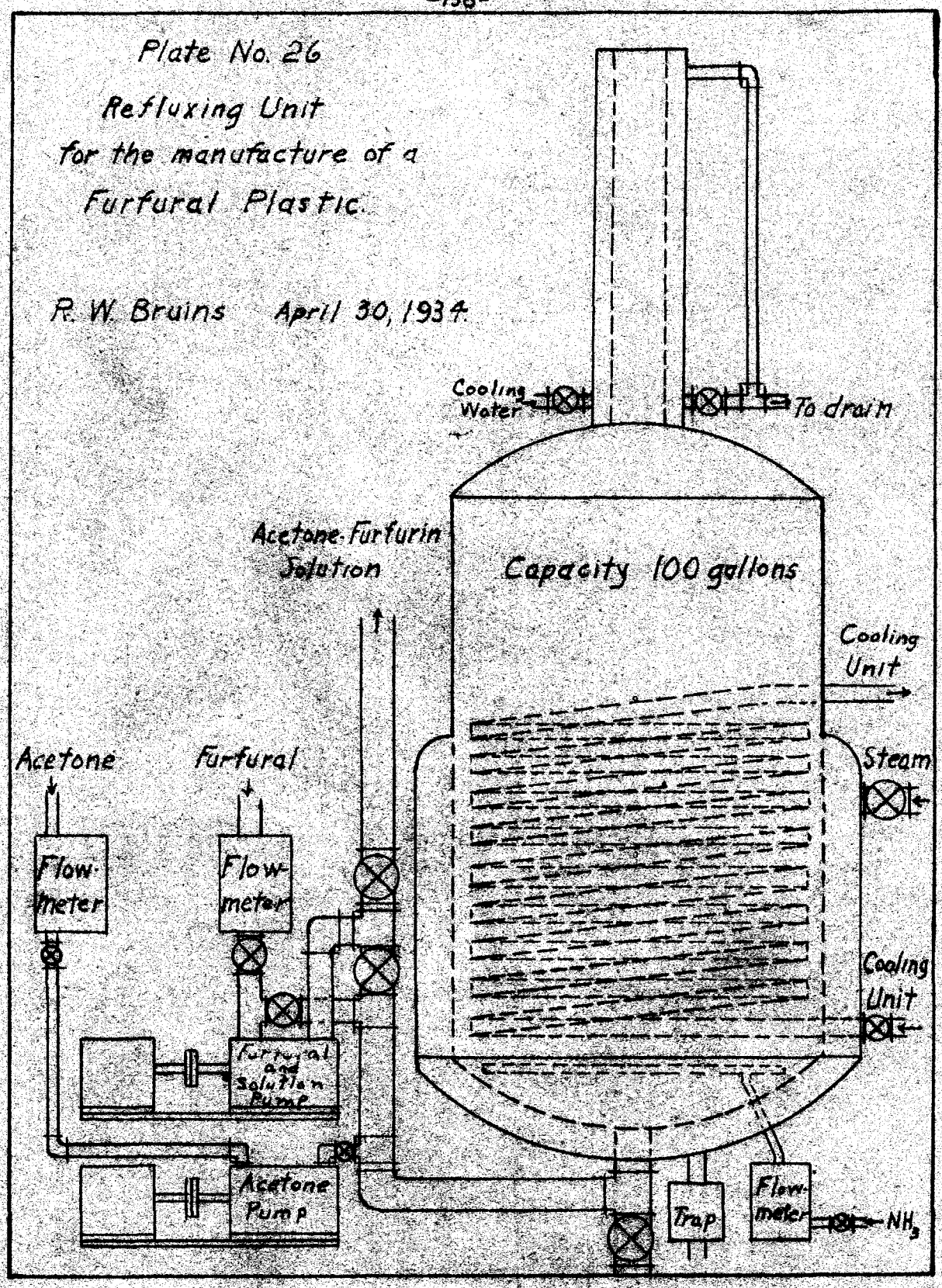
The process by which the molding compound is made is divided into two steps; first, the addition of ammonia to furfural to form the furfurin solution, and the refluxing of the furfurin solution with acetone; second, the addition of sulphuric acid to the furfurin-acetone solution to form the liquid molding material. Each step of the process will be carried out in a separate unit, so that two units will be required; the first, to produce the furfurin-acetone mixture, and the second, to mix the furfurin-acetone solution with acid to produce a liquid suitable for molding purposes.

The first unit handles the furfural and acetone, hence must have a capacity of 854 gallons of material per 24 hours. The unit (see plate No. 26) produces the furfurin-acetone

Plate No. 26

Refluxing Unit
for the manufacture of a
Furfural Plastic.

R. W. Bruins April 30, 1934.



solution by a process which requires two hours for completion. The following cycle is proposed: (1) fill tank with furfural (five minutes); (2) heat to 110 °C. (fifteen minutes); (3) treat with ammonia to form the furfurin solution (thirty minutes); (4) cool to 60 °C. (fifteen minutes); (5) turn on reflux and pump in acetone (five minutes); (6) reflux (twenty minutes); (7) cool to 25 °C. (fifteen minutes); (8) pump to storage and drain reflux column (five minutes). This two hour cycle permits twelve cycles per twenty four hours, hence the equipment should be large enough to handle seventy five gallons in one charge. To permit the use of equipment of standard commercial size, a one hundred gallon unit is specified.

The main feature of the unit is the 100 gallon kettle, which is equipped with a steam jacket, reflux condenser, and a cooling coil. The liquids are handled by centrifugal pumps. By a suitable arrangement of piping and valves, it is possible to make one pump do double duty, and handle both the raw furfural and the final solution. This pump has a capacity of twenty gallons per minute. The acetone pump is smaller, since it handles about seven gallons of acetone per charge; a pump having a capacity of 10 gallons per minute is specified. The volume of the liquids added is measured by means of flow meters. The ammonia is passed into the furfural through a perforated pipe in the bottom of the kettle, and is measured by means of a flow meter. Cooling of the liquid is accomplished

by a cooling coil connected to a mechanical refrigeration system. If desired, cold water could be circulated through the steam jacket to assist in the cooling.

The function of the second unit is to mix the furfurin-acetone solution with sulphuric acid to produce the liquid molding material. Since this mixing is attended by the evolution of heat, the material must be cooled rapidly to prevent solidification before it is desired. After the cooling, fillers may be added to the liquid, which process necessitates a suitable mixer.

The several pieces of equipment comprising the second unit are mounted on an angle-iron framework. At the top of the unit are two tanks from which the sulphuric acid and furfurin-acetone solution are withdrawn as needed. By placing these tanks at the top of the unit, the materials flow by gravity through the rest of the process, and no pumping is required. The furfurin-acetone solution tank has a capacity of two hundred and fifty gallons, which is sufficient to hold three charges from the first unit. The use of this size of tank permits the accumulation of sufficient furfurin-acetone solution to insure continuous operation of the unit, even if the equipment for making the solution were shut down for a few hours. The tank provided for the sulphuric acid has a capacity of fifty gallons; since eighty five gallons of acid are required daily, this tank will have to be filled twice every twenty four hours. The furfurin-acetone tank

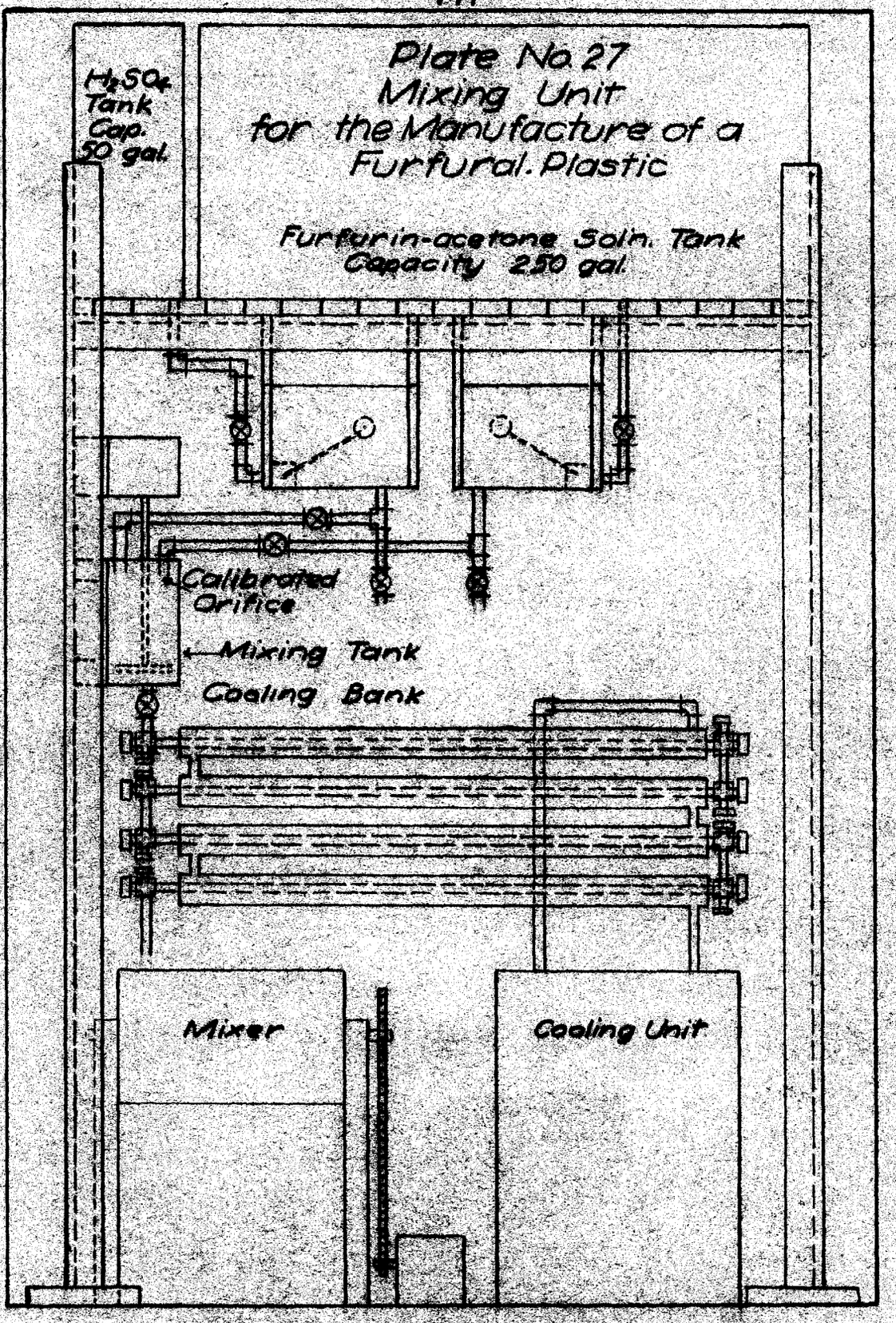


Plate No. 27
Mixing Unit
for the Manufacture of a
Furfural-Plastic
H_2SO_4 Tank Cap. 50 gal.
Furfurin-acetone Soln. Tank
Capacity 250 gal.
Calibrated Orifice
Mixing Tank
Cooling Bank
Mixer
Cooling Unit

is filled by means of the solution pump in the first unit; a small Duriron acid pump having a capacity of five gallons per minute is specified for pumping the acid from storage to the acid tank in the second unit.

When the furfurin-acetone solution is mixed with acid, it solidifies in a short time. Because of this fact, it is essential that the plastic should be mixed as needed, and should not be allowed to accumulate. A continuous system was designed to measure, mix, and cool the materials; since the equipment in this part of the unit is small, the amount of material present at any one time is small, and is handled so rapidly that it does not have time to solidify while in the unit.

The sulphuric acid and furfurin-acetone solution are measured by means of calibrated orifices, and in order to get a uniform flow through the orifice, a constant head is required. The constant head is supplied by a head-box, into which the flow of liquid from the storage tank is regulated by a valve controlled by a float. This arrangement insures a constant level of liquid in the head-box, and as a result there is a constant head at the orifice. The valve in the line from the head box to the orifice is the means by which the unit is controlled; if sufficient material has been mixed, these two valves are closed, and in a short time all the liquid has drained out of the mixing equipment. The unit can therefore be shut down without having an accumulation of liquid material.

The furfurin-acetone solution and sulphuric acid flow from their respective orifices into a mixing tank equipped with a motor driven stirrer. The mixing tank has a capacity of one gallon, and in operation is kept about half full by a suitable opening of the valve through which the liquid mixture is removed. This procedure is followed so that the materials stay in the mixing tank long enough to be thoroughly mixed. The stirring mechanism operates at a relatively low speed, so that while thorough mixing is obtained, no air will be mixed into the liquid.

The liquid material flows from the mixing tank through a cooling bank, where it is cooled by means of a mechanical refrigeration system to a temperature of 30 °C. The cooling bank is constructed to permit the tubes through which the liquid flows to be easily cleaned. If the mixing and cooling system is flushed out with water when the unit is shut down, a less frequent cleaning of the tubes will be required. The mixing and cooling equipment is constructed of Duriron, or some other corrosion resistant alloy which is not attacked by sulphuric acid.

The material flows from the cooling bank ready for use, unless it is desired to incorporate fillers. In this case, the liquid is poured into mixing equipment, and the filler added, care being taken to mix in as little air as possible, as the included air results in bubbles in the solidified material.

The mixer is mounted on trunnions, which permit tilting of the mixer to discharge the material, or it may be withdrawn through a valve at the bottom of the mixer.

CONCLUSIONS

The study of the application of furfural and its derivatives in the production of plastic materials has led to the following conclusions.

1. A plastic material may be produced by the polymerization of furfural treated with hydrogen sulphide with sulphuric or hydrochloric acid. The liquid molding material is produced when 15 parts of concentrated hydrochloric acid are added to 100 parts (by volume) of furfural treated with hydrogen sulphide for one hour. The liquid should be cooled to 30 °C. before molding. The material produced after solidification is hard, black, glossy, and has a tensile strength of about 800 pounds per square inch. It has a tendency toward cracking after removal from the molds.

2. The characteristics of the furfurin-furfural plastic are improved by the addition of furfural treated with hydrogen sulphide. Plastics having a tensile strength exceeding 1000 pounds per square inch may be obtained by polymerizing a mixture of 50 parts (by volume) of furfurin solution and 30 parts furfural treated with hydrogen sulphide for one hour, with 20 parts of concentrated hydrochloric acid. The material is not resistant to cracking.

3. The addition of small amounts of various compounds to the furfurin-furfural plastic as catalysts did not result in the discovery of any which exhibited the ability to catalyze

the reaction. Sodium tungstate and gallic acid were found to cause a slightly more rapid solidification. Ferrous ammonium sulphate decreased the tendency of the plastic toward cracking to a small degree. Of twenty metallic chlorides added as catalysts, manganous and ammonium chlorides were the only ones found to have any beneficial effect. These two chlorides decreased the cracking tendency of the plastic slightly.

4. In the preparation of the furfurin solution, a determination of the specific gravity of the solution can be used to indicate the point at which a 20% solution has been produced.

5. Dibutyl phthalate is of value as a plasticizing agent for furfural resins. Since it is immiscible with water, acids must be used which contain no water, or a solution of an acid in some solvent other than water, such as acetone or alcohol.

6. A resin having good tensile strength and little tendency toward cracking may be produced by the addition of acetone to the furfurin-furfural plastic. Good resins are formed by the addition of 20 parts of acid-acetone mixture to 100 parts (by volume) of furfurin solution. The acid-acetone mixture is formed by the addition of 80 parts of concentrated sulphuric acid to 100 parts of acetone.

7. Resins having a tensile strength in excess of 1000 pounds per square inch and practically no tendency toward cracking

may be obtained by refluxing 10 parts of acetone with 100 parts furfurin solution and polymerizing the refluxed solution with 10 parts of concentrated sulphuric acid per 100 parts of refluxed solution (by volume).

8. Tanks produced from the refluxed acetone-furfurin-furfural resin using asbestos as a filler show marked resistance to chemical corrosion. Solutions of caustic, and sulphuric, hydrochloric, and even hydrofluoric acids do not cause corrosion. The tanks absorb the solutions to some degree, and crack when they dry. For this reason the tanks should not be allowed to dry if they have contained a solution, but should be kept wet.

9. A soft carbon-like material may be produced by the polymerization of furfural treated with sulphur dioxide with hydrochloric acid. The optimum amount of sulphur dioxide is 8 grams per 100 grams of solution. The density of the plastic may be varied by controlling the amount of acid used.

10. A set of crayons having a range in hardness may be produced by polymerizing a mixture of furfural treated with sulphur dioxide and furfural treated with oxygen for two hours with hydrochloric acid. The optimum mixture is 60 parts SO_2-furfural, and 40 parts O_2-furfural, by volume. The hardness is controlled by adding hydrochloric acid in appropriate amounts. The hardness is decreased by using larger amounts of acid.

11. A plant for the production of the acetone-furfurin-furfural plastic has been designed.

SUMMARY

The utilization of agricultural waste materials has been studied along several lines in the laboratories of the Chemical Engineering Department and Engineering Experiment Station of Iowa State College. One of the methods developed by which agricultural byproducts such as oat hulls and corncobs are utilized is the production of furfural, which is obtained by the acid hydrolysis of the pentosan content of the various wastes. Furfural and its derivatives are susceptible to polymerization, which tendency has been utilized in the production of an interesting group of resinous materials.

The treatment of furfural with anhydrous ammonia results in the formation of a solution of furfurin in furfural. A solution of twenty grams of furfurin per one hundred grams of solution has been found to be best suited for the formation of resins. Addition of hydrochloric or sulphuric acid to this solution causes the polymerization and solidification of the liquid, the rapidity with which the change takes place being dependent upon the amount and kind of acid added. The solid material is black, hard, and has a high luster. The material is quite acidic, due to the acid used to produce polymerization, and has a tendency toward cracking and shrinking, which defect renders the fabrication of articles other than very small pieces impossible. The plastic has been made the subject of a series of experiments in an endeavor to find some method by which the defects of the material could

be corrected, and to adapt the plastic to the fabrication of molded products.

The treatment of an aqueous solution of furfural with hydrogen sulphide results in the formation of a colloidal solution of furfural polysulphide. Experiments were conducted to determine if the treatment of pure furfural with hydrogen sulphide could be used in the production of a molding material. A black, hard, shiny resin was produced by bubbling hydrogen sulphide through furfural at 110 °C. for one hour, and polymerizing this solution by the addition of concentrated hydrochloric acid in the ratio of 15 parts of hydrochloric acid to 100 parts of furfural treated with hydrogen sulphide by volume. This material had a tensile strength of about 800 pounds per square inch, but cracked within a short time after removal from the mold. A mixture of furfurin solution and furfural treated with hydrogen sulphide was used. A mixture of 50 parts (by volume) of furfural treated with hydrogen sulphide for one hour, 30 parts furfurin solution, and 20 parts concentrated hydrochloric acid resulted in a material having a tensile strength of 850 pounds per square inch. This compound also cracked after removal from the mold. The cracking can be prevented by coating the articles with paraffin, so as to prevent contact with the air.

Tests were made of numerous compounds to determine their ability to cause polymerization of the furfurin solution in a

catalytic way, and to discover if their addition would produce a material less susceptible to cracking. Of these compounds, sodium tungstate and gallic acid produced a slightly more rapid solidification. The addition of small amounts (2% by weight) of ferrous ammonium sulphate decreased the cracking tendency slightly, as did manganous and ammonium chlorides. Silicon tetrachloride was tested as a polymerizing agent, and was found to be capable of producing a hard, very brittle resin when added in the ratio of eight parts silicon tetrachloride to one hundred parts of furfurin solution, by volume. The polymerizing action of the silent electric discharge was tested, but did not result in the formation of a solid material.

The introduction of anhydrous ammonium into furfural is accompanied by an increase in the specific gravity of the solution. This increase of specific gravity is of interest, since it permits a determination of the concentration of the furfurin solution by obtaining the specific gravity of the solution and reading the corresponding concentration from a suitable table.

The properties of many resins are improved by the addition of a plasticizer. Dibutyl phthalate was added to the furfurin solution-acid mixture, in the hope that the phthalate would have a plasticizing action. Due to the compound's immiscibility with the aqueous acid used, the phthalate separated from the mixture and rose to the surface. The problem of getting

a homogeneous mixture was solved by the use of non-aqueous solutions of hydrochloric acid, such as an alcoholic solution. The resins produced using furfurin solution, dibutyl phthalate, and a solution of hydrochloric acid in butyl alcohol were hard, glossy, and had a lower density than the furfurin solution-aqueous hydrochloric acid resins. A slight tendency to crack was observed, although in numerous instances samples were obtained which were free from cracking.

Acetone was substituted for butyl alcohol as a solvent for hydrochloric acid gas. The resins produced by the polymerization of furfurin solution by a solution of hydrochloric acid in acetone were better than any previously produced. The tensile strength was not as high as that of other furfural resins, but its freedom from cracking was a quality which had not been observed in any other resin. Sulphuric acid was mixed with acetone, and the mixture added in various proportions to the furfurin solution. An acetone-sulphuric acid mixture of 80 parts sulphuric acid to 100 parts acetone by volume was found to give excellent results when added to the furfurin solution in the ratio of 20 parts of acetone-acid mixture to 100 parts of furfurin solution.

A step farther in the use of acetone was to reflux the acetone and furfurin solution, and add acid to the refluxed mixture. This procedure resulted in a still more improved resin. The best formula for the production of this resin

after numerous trials of different acid, acetone, and furfurin solution ratios is: (1) Reflux a mixture of 10 parts of a 20% furfurin solution and 1 part acetone (by volume) for twenty minutes. (2) Cool to 30 °C. and add slowly with stirring one part of concentrated sulphuric acid to 10 parts (by volume) of the refluxed mixture. Cool rapidly to 35 °C., add fillers if desired, and place in molds. (3) Remove from molds as soon as solid enough to permit handling. Cracking of the material results if the article is permitted to remain in the mold for an extended period of time. The resin produced using the above formula without fillers has a tensile strength in excess of 1000 pounds per square inch. It is hard, glossy, does not crack, and is easily molded.

The refluxed acetone-furfurin solution plastic was used in the fabrication of small tanks. In this application of the resin seventeen grams of shred asbestos per one hundred cubic centimeters of liquid material was used as a filler. Two sizes of tanks were made; a small size, the inside dimensions of which were 7½ x 4½ x 4½ inches, with half inch walls, was first molded; later a larger tank, 18 x 6 x 6 inches, with a wall thickness of three quarters of an inch were produced. The outstanding feature of these tanks was their resistance to corrosion. Aqueous solutions of caustic, and sulphuric and hydrochloric acids did not corrode the material. Aqueous hydrofluoric acid was also kept in the tanks without damage by the acid. The resinous material did absorb

some of the liquid; when the tanks were emptied and dried, the evaporation of the absorbed solutions caused the walls of the tanks to warp to such an extent as to produce cracking. While this is a series defect, it can be avoided by keeping the tanks filled at all times.

The addition of sulphur dioxide to furfural results in a solution which is polymerized to a soft, porous material by the addition of hydrochloric acid. The softness of the material enables it to be used as a crayon. The optimum amount of sulphur dioxide was found to be eight grams per one hundred grams of solution. The correct amount of hydrochloric acid is dependent upon the hardness desired; an increase in the amount of acid used decreases the hardness. The addition of furfural treated with oxygen was found to produce beneficial results. The treatment with oxygen consisted of bubbling the gas through furfural heated to a temperature of 110 °C. An excellent group of crayons may be produced by mixing six parts of an eight percent sulphur dioxide in furfural solution with four parts of furfural treated with oxygen for two hours (by volume). This mixture is polymerized with amounts of concentrated hydrochloric acid varying from ten to one hundred percent of the amount of furfural mixture used. By varying the acid used in ten percent intervals, a series of ten crayons having an excellent gradation in hardness is obtained. The crayons compare favorably with the charcoal

pencils used for sketching purposes.

A plant for the production of the refluxed acetone-furfurin solution plastic has been designed. The plant is divided into two units, the first of which produces the furfurin solution and refluxes it with the correct amount of acetone. The second unit is designed to continuously mix the sulphuric acid and refluxed acetone-furfurin solution in the desired ratio, and to cool the mixture rapidly to its molding temperature. Mixers are provided for the incorporation of fillers, if they are desired.

The author wishes to take this opportunity to express his appreciation to those who have assisted him in the course of this work. He is indebted to W. D. McKinley and G. T. Peterson, who as senior students did research on this work.

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The development of a furfural plastic.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1930)

The electrical properties of the plastic, the use of solvents as a method of removing excess acid and a determination of ammonia are presented.

2. Bakelite Corporation.

Synthetic resins from cresol and furfural.

Brit. Pat. 326,884 (1928). Abstracted in C. A. 24: 4945. (1930) Original not seen.

An intermediate resinous condensation product is first formed from cresol and furfural in the presence of a limited amount of basic condensing agents such as $Ca(OH)_2$ under reflux, which forms a product non-brittle on cooling. The resin is then transferred to an open mixing kettle and the reaction finished with more condensing agent.

3. Bakelite Corporation.

Resinous condensation product.

Brit. Pat. 359,047 (1930). Abstracted in C. A. 26: 6167 (1932). Original not seen.

Resinous products are obtained by condensing cresol or phenol with furfural in proportions to yield a reactive resin, and adding an accelerator comprising an alkaline earth metal oxide such as CaO or MgO and a methylene containing substance such as hexamethylene tetramine--the latter forming about 2% of the reaction mixture.

4. Beckman, E. and Dehn, E.

Einwirkung von Furfurol auf Phenole.

Sitzb. kgl. preuss. Akad. K. Wissenschaften; Jahrg. 1918: 1201-21 (1918). Also reviewed in Ellis, C. A. Synthetic Resins and their Plastics; P. 201-21. Chemical Catalog Co., New York. (1923)

5. Bruins, Paul F.

The commercial utilization of agricultural wastes.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1927)

Furfural is proposed and tested for various uses, in particular its use as an ingredient in the preparation of embalming fluids. Tests are performed with veterinary specimens.

6. Bruins, Paul F.

The application of furfural and its derivatives to the manufacture of plastics.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1930)

The discovery and initial work on the furfurin-furfural plastic are presented.

7. Bruins, R. W.

The physical properties of a furfural plastic.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1930)

The effect of fillers, and the use of several different polymerizing agents are given. Several methods of curing the plastic were tested.

8. Bruins, R. W.

The development of a furfural plastic.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1931)

A means of preventing cracking is proposed, and the use of oxygen is studied. A machine for the production of golf tees is designed.

9. Campbell, D.

Casein-furfural plastics.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1926)

Milk casein and furfural reac t under heat and pressure to form a plastic material.

10. Cherry, O. A. and Kurath, F.

Composition of matter and process of producing same.

U. S. Pat. 1,800,815 (1931). Abstracted in C. A. 25: 3503 (1931). Original not seen.

By the reaction of an aldehyde such as furfural on reaction products such as those formed from stearic acid and aniline or similar components, products are obtained which are waxy and may be used as plasticizing agents.

11. Cherry, O. A. and Kurath, F.

Potentially reactive phenolic condensation product and process of producing same.

U. S. Pat. 1,857,357 (1932). Abstracted in Official Gazette, U. S. Pat. Office 418: 372 (1932). Original not seen.

The product formed by heating furfural with a phenolic compound such as cresylic acid is further heated with methylene containing substances such as formaldehyde solution sufficient to form a fusible reaction product and to supply enough additional CH_2 groups to render the fusible product potentially reactive. Furfuramide is added to fix the additional CH_2 groups in resinous layer, and water is discharged.

12. Claisen, L. and Ponder, A. C.

Ueber die Condensation der Aldehyde mit Phenolen und aromatischen aminen.

Annalen der Chemie 273: 261-74. (1887)

A yellow oil is produced by the reaction of acetone and furfural in the presence of aqueous alkaline solutions.

13. Dobereiner, J. W.

On the medicinal and chemical uses and properties of formic acid.

Annalen der Chemie 3: 141 (1832).

A yellow oil is obtained in an attempt to prepare formic acid by the action of sulfuric acid and manganese dioxide on sugar.

14. Eichwald, E.

Process for purifying oils and the like.

U. S. Pat. 1,550,523 (1925). Official Gazette, U. S. Pat. Office 537: 691 (1925). Original not seen.

Furfural is used in a process for purifying hydrocarbon oils.

15. Ellis, C.

Molded articles from nitrocellulose and furfural.

U. S. Pat. 1,558,442 (1925). Abstracted in C. A. 20: 290 (1926) Original not seen.

An acidulated solution of nitrocellulose in furfufal is poured into molds and permitted to harden.

16. Ellis, C.

Furfural resin composition and process of making same.

U. S. Pat. 1,771,033 (1930). Abstracted in C. A. 24: 4648 (1930). Original not seen.

Furfural and phenol are combined in a mol to mol ratio in the presence of Na_2CO_3 at a temperature above 100 °C. until the mixture becomes resinous. Hexamethylene tetramine and some fixed alkali are then added.

17. Evans, W. V. and Aylesworth, M. B.

Some critical constants of furfural.

Ind. and Eng. Chem. 18: 24-7 (1926).

The refractive index of furfural is found to be 1.52608 for the D line of sodium.

18. Graft, F.

Phenol resin and process of making same.

U. S. Pat. 1,693,112 (1929). Abstracted in Official Gazette, U. S. Pat. Office 376: 919 (1929). Original not seen.

A phenol such as phenol is caused to react with furfural in proportions to yield an infusible resin. The reaction is arrested before the infusible state is reached and the mass is heated to dehydrate the resin and advance it. A hardening agent such as hexamethylene tetramine is used.

19. Hall, L. P.

A furfural plastic.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1929)

The effect of the time of treatment with ammonia, the use of technical or redistilled furfural, the use of hydrochloric acid gas as polymerizing agent and the use of fillers are presented.

20. Harris, W. D.

Cellulose-pentosan plastics.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1931)

An investigation is made of the corncob-phenol resin. Soluble sugars are found in the resin, and are cited as possible causes for water absorption.

21. Herzog, W. and Kreidl, J.

Studien über den Zusammenhang zwischen Verharzungsfähigkeit und Konstitution chemischer Verbindungen.

Z. angew. Chem. 35: 465-7. (1922). Also reviewed in Ellis, C. Synthetic resins and their plastics, P. 229. Chemical Catalog Co. New York. (1923)

A discussion of condensation products containing the $-C=C-C-C-$ grouping is presented.

22. Hull, S. M.

Casein-furfural molding composition.

U. S. Pat. 1,711,025 (1929) Abstracted in C. A. 23: 3060 (1929) Original not seen.

Condensation of a dry protein such as casein and dry furfural is effected in the presence of a waterproofing material such as a rosin-glycerol ester to form a product suitable for molding.

23. Jaeger, A. O.

Purification of crude anthracene.

U. S. Pat. 1,693,713. (1928)

The use of furfural as a selective solvent in the purification of anthracene is presented.

24. Kaiser, H. E. and Hancock, R. S.

Process for recovering high grade wood rosin.

U. S. Pat. 1,715,084 (1929)

Furfuryl alcohol is used in a process for the purification of wood rosin.

25. Kaiser, H. E. and Hancock, R. S.

High grade wood rosin.

U. S. Pat. 1,764,085 (1929)

Furfural is used in a process for the purification of wood rosin.

26. Kappeler, H.

Urea-furfural condensation products.

Brit. Pat. 293,872 (1927) Abstracted in C. A. 23: 1729 (1929). Original not seen.

Black compounds like ebonite are produced by condensing furfural and urea with or without the use of catalysts or solvents. Other RCHO or amino compounds may be present. The condensation may

be carried out in steps; in the first step no catalyst or a neutral or alkaline catalyst may be used, and in the final stage an acid electrolyte or an ammonia salt may be used.

27. Kappeler, H.

Plastic compositions.

Swiss Pat. 133,702-12 (1927) Abstracted in C. A. 24: 476 (1930). Originals not seen.

Plastic masses may be obtained by the reaction of urea and furfural with one of the following: thiourea, aniline, alpha or beta naphthylamine or meta or para phenylenediamine. The reaction may take place in the presence of a solvent, diluent or catalyst.

28. Kappeler, H.

Plastic composition.

Swiss Pat. 133,387 (1927) Abstracted in C. A. 24: 476 (1930). Original not seen.

A black, infusible, insoluble plastic mass is obtained by the reaction of thiourea and furfural. A contact agent, diluent or solvent may be present during the reaction.

29. Kappeler, H.

Furfural condensation product.

Swiss Pat. 146,561 (1929). Abstracted in C. A. 26: 2287 (1932). Original not seen.

Furfural is treated with acetic acid in the presence of acid condensing agents. The product is a hard gum-like mass resistant to acids and alkalies. It can be used for impregnating purposes before setting to a solid.

30. Kappeler, H.

Artificial substances.

French Pat. 697,169. (1930) Abstracted in C. A. 25: 2822 (1931). Original not seen.

Infusible substances are prepared by condensing furfural or its derivatives with other aldehydes and their polymers with or without solvents or diluents, in the presence of acid condensing agents.

31. Kappeler, H.

Aldehyde condensation product and process of making same.

U. S. Pat. 1,873,599. (1932) Abstracted in C. A. 26: 6081 (1932). Original not seen.

An infusible black reaction product is obtained by reaction of furfural with other aldehydes such as acetaldehyde, paraaldehyde, formaldehyde, benzaldehyde and crotonaldehyde in the presence of an inorganic acid such as hydrochloric acid.

32. Losanitsch, S. M.

Ueber die Elektrosynthesen.

Ber. 40: 4656-66. (1907)

The silent electric discharge is found to have a polymerizing action on several compounds.

33. Mains, G. H. and Phillips, M.

Some synthetic resins from furfural.

Chem. Met. Eng. 24: 661-3. (1921)

Various furfural resins are prepared by reaction with ketones, amines and amides.

34. Mains, G. H.

Resinous condensation product.

U. S. Pat. 1,841,138. (1932) Abstracted in Official Gazette, U. S. Pat. Office 414: 523 (1932). Original not seen.

The reaction product of furfural with a phenolic compound is used with a solvent and a solution of china wood oil in furfural in such proportions that fibrous sheets such as paper impregnated with the compound and then dried will not adher to each

at ordinary temperatures, but will be free from dust and suitable for molding.

35. Matlack, J. D.

The impregnation of cornstalk board with synthetic resins.

Unpublished thesis; library, Iowa State College, Ames, Iowa. (1933)

Synthetic lumber produced from cornstalks is impregnated with various synthetic resins and hot molded under pressure to produce panel board of good properties and appearance.

36. Meunier, G.

Application of furfural to the manufacture of varnish resins.

Mat. grasses. 9: 4516-7. (1916). Abstracted in C. A. 10: 2805 (1916). Original not seen.

Furfural yields a black varnish resin in a reaction with aniline or acetone.

37. Meunier, G.

Condensation product.

French Pat. 472,384 (1916). Abstracted in C. A. 10: 280. (1916) Original not seen.

Yellow condensation products are formed by the reaction of furfural and acetone with the use of alkaline catalysts.

38. Moss, W. H. and White, B.

Synthetic resins.

Canadian Pat. 303,697 (1930). Abstracted in C. A. 24: 5518 (1930). Original not seen.

A synthetic resin may be prepared by the reaction of furfural and para toluene sulfonamide. Three percent of a catalyst such as soda ash is used. The mass is heated at 150 °C. for eight hours.

39. Norton, R. A.

Purification of crude anthracene.

U. S. Pat. 1,764,031 (1930).

The use of tetrahydrofurfuryl alcohol as a selective solvent in the purification of anthracene is presented. The use of any hydrogenated furfuryl alcohol is claimed.

40. Novotny, E.

Moldable composite body.

U. S. Pat. 1,389,147 (1931).

A method for making laminated material suitable for phonograph records, using furfural-phenol resin.

41. Novotny, E. and Kendall, D.

Phenol resin and process of making same.

U. S. Pat. 1,705,493 (1929) Abstracted in Official Gazette, U. S. Pat. Office 380: 564 (1929). Original not seen.

Phenol and furfural are heated together under such conditions (temperature of 350 °F. or lower) that all materials enter into combination and form a soluble fusible resin, which is further heated to convert it to an insoluble infusible compound.

42. Novotny, E. and Kendall, D.

Synthetic resin composition.

U. S. Pat. 1,705,496 (1929). Abstracted in Official Gazette, U. S. Pat. Office 380: 565 (1929). Original not seen.

In forming a potentially active resin phenol and furfural are heated after mixing in the proportion of 100 parts cresol to 75 of furfural, as to insure complete reaction in the presence of potassium carbonate, 2 parts. Water is removed. Furfuramide is added as a hardening agent.

43. Novotny, E.

Furfural-urea resin and process of making same.

U. S. Pat. 1,827,824 (1932) Abstracted in Official Gazette, U. S. Pat. Office 411: 624 (1932). Original not seen.

A plastic resinous condensation product of furfural and urea or a derivative is obtained by heating with an acid or basic catalyst. The resin is suitable for heating further to produce an infusible material.

44. Phillips, M.

Resinous condensation product of lignin and furfural.

U. S. Pat. 1,750,903 (1930).

By condensation in the presence of hydrochloric acid, products are obtained which are of resinous character and of black color.

45. Richardson, L. T.

Furfural-acetone resins and method of making same.

U. S. Pat. 1,584,144. (1926)

Molded articles are produced by the addition of an acid condensing agent and fillers to a resin produced by refluxing acetone and furfural with an alkaline catalyst, and molding the mixture under heat and pressure.

46. Richardson, L. T.

Synthetic resins and method of producing same.

U. S. Pat. 1,682,934 (1928).

Furfural and an inorganic substance of acid reaction, preferably sulphuric acid are caused to react.

47. Snell, H. S.

A molding compound.

U. S. Pat. 1,678,713 (1928)

A material which may be used as a dielectric is formed by the condensation of furfural and an insoluble proteinate such as aluminum soybean or milk caseinate.

48. Stenhouse, J.

Ueber das sogenannte künstlich Ameisenol.

Annalen der Chemie 35: 301 (1840).

Furfural is prepared by the action of sulphuric acid on sawdust and oatmeal. Gums and resins are formed when furfural is boiled with acids and alkalies.

49. Sweeney, O. R.

The commercial utilization of corncobs.

Iowa Eng. Exp. Sta. Bul. 73. P. 74-81. (1924)

A furfural-phenol molding compound is formed by treating corncobs with phenol in the presence of an acid. The furfural is produced by an acid hydrolysis of the corncobs. The spent cobs serve as a filler.

50. Trickey, J. P., Miner, C. S. and Brownlee, H. J.

Furfural resins.

Ind. and Eng. Chem. 15: 65-6. (1923).

The effect of alkaline and acid catalysts on the furfural-cresol reaction is studied.

51. Trickey, J. P. and Miner, C. S.

Process for making furfural resins.

U. S. Pat. 1,665,233 (1928).

In forming a resinous product furfural is treated with various metallic salts.

52. Trickey, J. P. and Miner, C. S.

Furfuralcohol resins.

U. S. Pat. 1,665,235 (1928)

An infusible and insoluble final resinous product is obtained from furfuryl alcohol by heating with a small quantity of hydrochloric acid.

53. National Research Council.

International Critical Tables of Numerical Data.

McGraw-Hill Book Co., Inc. New York.

a.	Density	Vol. 1: 190	(1926)
b.	Melting point	1: 190	(1926)
c.	Dielectric constant	6: 88	(1929)
d.	Boiling point	1: 190	(1926)

VITA

I was born in Milwaukee, Wisconsin, on March 27, 1910. My father was Dr. Henry Martin Bruins, a Presbyterian minister. He was of Dutch descent, his parents having emigrated from The Netherlands to Alto, Wisconsin, in 1845. My mother's maiden name was Lillian Fastenau, whose parents came from Germany, and after coming to the United States, made their home at Pekin, Illinois.

I attended the public schools of Milwaukee from 1915 to 1917. In the latter year the family moved to Pella, Iowa, where my education in the public schools was continued until 1926, at which time I graduated from high school. I then attended Central College, at Pella, Iowa, for two years, and enrolled at Iowa State College in the fall of 1928. The Bachelor of Science degree in Chemical Engineering was conferred in 1930, and the Master of Science degree in 1931, by Iowa State College.

My major work has been conducted in the field of Chemical Engineering under the direction of Dr. O. R. Sweeney. Other work in Chemical Engineering has been taken under Drs. F. C. Vilbrandt and H. A. Webber; in Chemistry, under Drs. F. E. Brown, J. A. Wilkinson, Henry Gilman, E. I. Fulmer and L. M. Christensen; and in Mechanical Engineering, under Profs. R. E. Roudebush, W. H. Meeker, M. P. Cleghorn and R. A. Norman.